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**ELECTROLYTIC METHODS OF ANALYSIS IN**

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**VOLUMETRIC CHEMICAL ANALYSIS.** By J. B.

COPPOCK, Lecturer in Chemistry, Bath Technical School.

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WHITTAKER & CO., London, E.C.

OUTLINES  
OF  
PHYSICAL CHEMISTRY

BY  
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PROFESSOR OF CHEMISTRY IN THE UNIVERSITY OF BRUSSELS

TRANSLATED FROM THE FRENCH, WITH THE AUTHOR'S PERMISSION

BY

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*WITH 52 ILLUSTRATIONS*

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DEDICATED TO THE MEMORY OF

Dr. F. HURTER

CHIEF CHEMIST AND SCIENTIFIC ADVISER

TO THE UNITED ALKALI COMPANY





# AUTHOR'S PREFACE

TO

THE ENGLISH EDITION

---

ORIGINALLY published in French,<sup>1</sup> this small book had the good fortune to attract the attention of the late Dr. F. Hurter, who in April 1897 secured the right of translation. This distinguished chemist, owing to the pressure of technical work, had only translated the first two parts of the book when his untimely death at the beginning of 1898 brought his labours to a close and robbed me of my friend and collaborator.

The work thus interrupted was later taken up by Dr. J. McCrae, but as in the interval I had recognised the necessity of modifying many passages in the book and even of entirely rewriting many chapters (particularly in the first half) my new collaborator could make little use of the translation prepared by Dr. Hurter and found himself confronted with a totally new task.

The work now proceeded more rapidly than before, and during the University vacation the revision of the original

<sup>1</sup> By H. Lamertin, Brussels, 1897.

## ADDENDA

1. Add to first footnote on p. 46 :—Glass flasks and tubes (*Dewar* tubes) constructed on the same principle are also used.

2. Add to § (c) on p. 97 :—We now know a few other substances active both in solution and in the crystalline state: rubidium tartrate, caesium tartrate, cinchonine antimonyl tartrate, zinc bimalate, patchouli camphor, and one or two more substances.

3. Addition to the method of determining the conductivity of electrolytes, pages 197–199 :—*Stroud and Henderson* ('Phil. Mag.,' 43, 19) have invented a method of measuring the conductivity of electrolytes by direct currents (80 volts) in which the effects of polarisation are eliminated by introducing into each of two arms of a Wheatstone bridge cells containing different lengths of solution. In the arm containing the shorter cell there is a resistance in series with this cell, which in the position of equilibrium is equal to the difference in the lengths of the electrolyte in the two cells.

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# OUTLINES OF PHYSICAL CHEMISTRY

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## FIRST PART *FUNDAMENTAL THEORIES*

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### LAWS OF CHEMICAL COMBINATION AND THE ATOMIC HYPOTHESIS

FOLLOWING the example of *Boyle*<sup>1</sup> and of *Lavoisier*,<sup>2</sup> we apply the term *elementary* to those substances which the chemist is unable to split up into simpler constituents. The substances submitted to our researches only rarely merit this appellation. In the majority of cases we deal with substances which are formed by the union of two or more elements, and constitute *chemical compounds*.

The formation of these compounds takes place according to well-defined laws :

1. *The Law of Weight*.—The weight of a compound is equal to the weight of the elements which have united to form it.

---

<sup>1</sup> *The Sceptical Chymist*, 1661.

<sup>2</sup> *Nomenclatura chimique*, Lavoisier, Berthollet et Fourcroy, 1787.

2. *The Law of Constant Proportions*.—In order to form a substance, it is always necessary to have the same elements united in the same proportions.

3. *The Law of Multiple Proportions*.—When two elements can unite in several different proportions to give distinct compounds, there is always a simple numerical relation between the different quantities of one of the elements which unite with the same quantity of the other element.

We may add :

4. *The Law of Reciprocal Proportions*.—The weights of different elements which unite with a constant weight of another element (taken as standard of comparison) express also, directly or after multiplication by a simple number, the proportional weights of these elements which combine amongst themselves.

These laws, which were known at the beginning of this century, still remain the exact expression of observed facts. They are best interpreted by the *atomic hypothesis*.

We assume that matter is made up of extremely small particles which we call *atoms*. The atoms constitute the limit of divisibility by chemical means, and exist in as many species as there are non-divisible substances (*elements*). Atoms may combine to form *molecules*. The molecule of a compound consists of atoms of different species. The molecule of an element may consist of a single atom, or it may be formed by the union of several atoms of the same species.

*The Atoms have a Fixed and Invariable Weight*.—With these ideas it is easy for us to comprehend the *raison d'être* of the above-mentioned laws.

In fact :

1. The weight of a molecule will be equal to the sum of the weights of the atoms which have united to form it. It is sufficient then to consider a conglomeration of  $n$  molecules, that is to say, a certain weight of a chemical compound, and we arrive at our first fundamental law.

2. The formation of any given molecule (the chemical individual of a substance) requires  $m$  atoms of one species,

$n$  atoms of another,  $p$  atoms of a third,  $m, n, p$  being invariable numbers. That is, the same elements must be united in the same proportions, as stated by the second law above.

3. If  $m$  atoms of one element can combine with  $n, 2n$ , or  $3n$  atoms of another element with formation of different substances, it is evident that the weights of the latter element will be in the ratio  $1 : 2 : 3$ , that is, in simple numerical relation.

There is no difficulty in expressing the law of reciprocal proportions in the same manner, *i.e.* in atomic language. In fact, the three first fundamental laws, based on the works of *Lavoisier, Berthollet, Proust*, and *Dalton*, have enabled the last-mentioned to establish the great probability of the real existence of atoms.<sup>1</sup>

If this book pretended to be a complete treatise on theoretical chemistry, there would have to be inserted here a very important chapter on 'The Determination of the Proportional Numbers' (also called equivalents or atomic weights according to the authors and the epochs of their discovery).<sup>2</sup> But for a study of this question, to which the most famous men of science, *Berzelius, Dumas, Stas*, and

<sup>1</sup> Dalton, *New System of Chemical Philosophy*, 1808-1810.

<sup>2</sup> The *equivalents* have on several occasions played an important part in the history of chemistry (Wollaston, 1814; Gmelin, about 1840). They were represented by the symbols of the elements, and were used to give a simple expression to the results of analytical researches and to the quantitative composition of various substances. The symbol of hydrogen represented *one part by weight* of this element, that of chlorine 35.5 parts, that of oxygen 8 parts. Similarly the equivalents of the following elements were expressed by their respective symbols, representing the following number of parts by weight: Br = 79.95; S = 16; N = 14; P = 31; C = 6; Si = 14; Al = 13.75; Fe = 28; Ca = 20; Mg = 12; Na = 23; K = 39.1; and so on.

The formula HO represented perfectly the quantitative composition of water: 8 parts of oxygen and 1 part of hydrogen. Sulphuretted hydrogen was represented by HS (16 parts of sulphur and 1 part of hydrogen). Sulphuric anhydride was written SO<sub>3</sub> (24 parts of oxygen and 16 parts of sulphur). In an analogous

others have devoted their wisdom and their patience, the reader is referred to the larger treatises on theoretical chemistry (such as that of *Ostwald*).

We may, therefore, pass on immediately to a systematic exposition of the fundamental theories. As these theories are now generally accepted, we need not devote so many pages to their discussion as will be required for a critical examination of certain comparatively recent doctrines, which are not so universally admitted.

## THE GASEOUS STATE

### *The Density of Gases and Vapours*

The gaseous state is characterised by an extremely feeble intermolecular attraction. A gaseous mass has neither a definite form nor a definite volume, but expands uniformly through any space which is placed at its disposal.

The volume of a gaseous mass is a function of its temperature and pressure.

*Boyle's Law*.<sup>1</sup> At constant temperature, the volume occupied by a gaseous mass is inversely proportional to the pressure to which the gas is subjected:

$$pv = p^1 v^1 = \text{constant.}$$

*Gay-Lussac's Law* (*Dalton's Law*).<sup>2</sup> Under constant pressure, the same rise in temperature produces in all gases the same increase in volume. All gases have the same coefficient of expansion by heat:

$$\alpha = \frac{1}{273} = 0.00367 \text{ of the volume at } 0^\circ\text{C.}$$

---

manner the following formulæ were interpreted:  $\text{HSO}_4$ ,  $\text{NH}_3$ ,  $\text{CO}_2$ ,  $\text{SiO}_2$ ,  $\text{CaO}$ ,  $\text{NaO}$ ,  $\text{FeO}$  &c. We see that these expressed quite perfectly the composition of sulphuric acid, ammonia, carbonic anhydride, silicic anhydride, lime, sodium oxide, ferrous oxide, &c. These formulæ had only the single purpose of showing as simply as possible the results furnished by analysis. They were to a great extent independent of all hypothesis and all theory.

Often known on the Continent as *Mariotte's Law*.

hence :

$$v = v_0 (1 + \alpha t).$$

If the temperature of a gas be raised without allowing it to expand, the pressure increases according to the formula :

$$p = p_0 (1 + \alpha t).$$

By combining these two equations we get the GENERAL EQUATION OF A GAS :

$$p v = p_0 v_0 (1 + \alpha t).^1$$

This equation can be arrived at directly from the following considerations. Let  $v_0$  be the volume of a gaseous mass at  $0^\circ$  and under the normal pressure  $p_0$  (76 centimetres of mercury), then the volume at  $t^\circ$  under the same pressure will be  $v_0 (1 + \alpha t)$ . Let the pressure be now reduced to 1 centimetre of mercury, then the volume will increase to  $v_0 (1 + \alpha t) p_0$ , and if the gas be now compressed to the pressure  $p$  the final volume will be

$$v = \frac{p_0 v_0 (1 + \alpha t)}{p}$$

$$\text{or } p v = p_0 v_0 (1 + \alpha t).$$

*Transformation of the General Equation :*

$$p v = p_0 v_0 (1 + \alpha t).$$

At  $t^\circ$ , the absolute temperature (counting from  $-273^\circ \text{C.}$ ) will be

$$T = 273 + t.$$

Therefore

$$t = T - 273.$$

$p$  = pressure } at the temperature  $t$ .  
 $v$  = volume }

$p_0$  = normal atmospheric pressure = 760 millimetres of mercury.

$v_0$  = volume at  $0^\circ$  under normal pressure.

If we introduce this value into the equation, we get :

$$p v = p_0 v_0 \left[ 1 + \frac{1}{273} (T - 273) \right] = p_0 v_0 \left( 1 + \frac{T}{273} - 1 \right) \\ = p_0 v_0 \frac{T}{273} = \frac{p_0 v_0}{273} T$$

For any given mass of gas, the value of  $\frac{p_0 v_0}{273}$  is a constant usually represented by  $R$ , so that we can give the general equation the simple form :

$$p v = R T.$$

N.B.—The numerical value of  $R$  depends on the unit of volume and unit of pressure chosen. We shall return to this subject.

#### *Determination of the density of a Gas or Vapour*

Having given a certain weight  $G$  of a gas, we have observe :

$v$ , its volume in cubic centimetres ;  
 $p$ , its pressure in millimetres of mercury ;  
 $t$ , its temperature in degrees Centigrade.

We have then all the data necessary for the calculation of the density of the gas, *relatively to air*.

Since  $p v = p_0 v_0 (1 + \alpha t),$

therefore  $v_0 = \frac{p v}{p_0 (1 + \alpha t)}$

will be the volume of the gas at  $0^\circ$  and under normal pressure. The same volume of air would weigh

$$0.00129 \frac{p v}{p_0 (1 + \alpha t)} \text{ grams,}$$

since one cubic centimetre of air at  $0^\circ$  and 760 millimetres pressure weighs 0.00129 grams.

Now, the gas under investigation weighs  $G$  grams; therefore, its density will be

$$G \div 0.00129 \frac{pv}{p_0(1+at)} = \frac{G(1+at)p_0}{0.00129pv}.$$

Several methods for the determination of  $G$ ,  $p$ ,  $v$ , and  $t$  have been proposed. *Dumas*, *Gay-Lussac*, and *Hofmann* have elaborated classical methods which are described in every text-book on physics. In chemical laboratories *V. Meyer's* DISPLACEMENT METHOD is preferably followed.

In the figure (fig. 1)  $A$  represents a reservoir of about 100 cubic centimetres capacity. The vertical tube,  $B$ , has an internal diameter of three to four millimetres, and the lateral branch,  $C$ , is a capillary tube. The interior of this apparatus is dried by means of a current of hot air then introduced into the bath  $D$ ; and the pneumatic trough  $E$  is so adjusted that the opening of the capillary tube is under water.

The bath contains a liquid whose boiling point is at least fifty degrees higher than the boiling point of the substance the vapour density of which is to

be determined. By means of a Bunsen burner, the flame of which can be easily regulated, the liquid in the bath is brought to boiling, so that the cylindrical bulb  $A$  is well enveloped in vapour. As the tube  $B$  is closed by a stopper, the air expelled by expansion escapes by the capillary tube and rises in bubbles through the water in the pneumatic

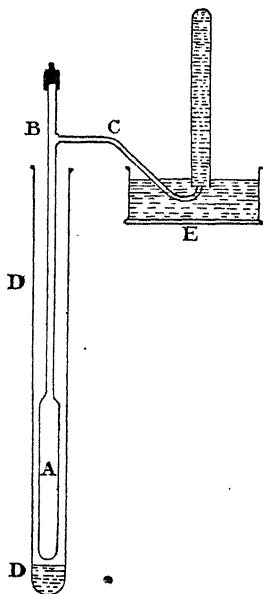


FIG. 1



trough. The end of this evolution of gas indicates the moment when a stationary temperature has been established in the whole apparatus. A measuring cylinder filled with water is then inverted over the end of the capillary tube. The tube B is now opened, a known weight of the substance is dropped in, and B at once closed again. The substance which has fallen to the bottom of A volatilises, and displaces the air. The superimposed layers of air are gradually expelled<sup>1</sup> and collected in the measuring cylinder, where finally a volume of air will have collected equal to the volume which would be occupied by the weight of the substance taken in the vapour state at the temperature of the water in the trough. The displacement of the air, as a rule, ceases sufficiently suddenly to indicate the end of the operation. The measuring tube is then transferred to a deep vessel filled with water, and so adjusted that the levels of the water inside and outside the tube are the same, then the volume is read off and the temperature and barometric pressure noted. We are then in possession of all the data ( $G$ ,  $v$ ,  $t$ , and  $p$ ) necessary for the calculation. To obtain exact results it is necessary to reduce the barometric pressure to  $0^\circ$  and to deduct from  $p$  the tension of aqueous vapour at  $t^\circ$ .

#### *Complementary Details and Remarks*

1. To facilitate the introduction of the substance and avoid opening the tube B, the top part of the apparatus is generally somewhat modified.
2. The weight of substance to be taken must be regulated by the consideration that its vapour must not fill more than a third of the bulb A; that is, it must only occupy about thirty cubic centimetres.
3. According to the degree of volatility of the substance, it is weighed in small open or closed bulbs (of glass or

---

<sup>1</sup> The displaced air, all along its path, is at the same temperature as those parts of the apparatus with which it is momentarily in contact.

of Wood's metal). If the bulb is sealed, the point is broken off just before it is allowed to fall into A.

Certain solids can be introduced without any bulb, in the form of compressed cylinders.

4. In order to prevent breakage by the fall of the small bulb a protective layer of asbestos is put into the bottom of A.

5. The substances most often employed for the heating bath are : chloroform, benzene, water, commercial xylene, aniline, ethyl benzoate, thymol, amyl benzoate, diphenylamine, phenanthrene, mercury, sulphur, &c. ; an air bath may also be used (*L. Meyer*). For working at very high temperatures the apparatus A B C is made of platinum or porcelain and is heated by means of a *Perrot* gas furnace (special model).

6. As some vapours are attacked by air it is necessary to fill the apparatus, before the experiment is made, with an indifferent gas, such as carbon dioxide, nitrogen, or hydrogen. In these cases a modified form of the apparatus is used.

7. It is to be noted that the dilution of a vapour by another gas favours the decomposition of molecular associations. Consequently, *V. Meyer's* method often leads to vapour densities which are smaller than those obtained by *Dumas' method*. Such is the case for aluminium chloride, sulphur, iodine at high temperatures, &c. (see the small book '*Die Praxis der Molekelgewichtsbestimmung*,' by *H. Biltz*, Berlin, 1898).

#### AVOGADRO'S HYPOTHESIS

GAY-LUSSAC'S LAW OF VOLUMES.—When two gases combine chemically, there is a simple ratio between the volumes which enter into reaction. If the compound formed is also a gas, its volume bears a simple ratio to the volumes of the constituents. For instance : one volume

of hydrogen and one volume of chlorine combine to form two volumes of hydrochloric acid gas. Two volumes of hydrogen and one volume of oxygen give two volumes of steam. Three volumes of hydrogen unite with one volume of nitrogen to give two volumes of ammonia.

Since experiment shows that there is a simple relation between the volumes of the gases which enter into reaction, and since it is, *a priori*, extremely probable that there is a simple relation between the numbers of atoms which combine with each other,<sup>1</sup> it follows that there ought to be a simple relation between the numbers of atoms which are contained in equal volumes of different gases.

One step further leads us to admit AVOGADRO'S HYPOTHESIS: *Equal volumes of different gases (measured at the same temperature and pressure) contain the same number of individual particles.* If this hypothesis is correct, then:

1. The densities of different gases must stand in the same relationship as do the weights of their gaseous particles.

2. The individual particles of elementary gases must not be confounded with their atoms. They are more often composed of several atoms, and their degree of divisibility can be experimentally determined.

For instance: One volume of hydrogen unites with one volume of chlorine to form two volumes of hydrochloric acid. If Avogadro's hypothesis be well founded, this means that the chlorine originally concentrated in  $n$  particles has now become distributed over  $2n$  particles. Consequently the individual particle of chlorine is divi-

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<sup>1</sup> In the case of chlorine and of hydrogen, for example, it is, *a priori*, very probable that the formation of a particle of hydrochloric acid gas results from the union of a small number of atoms of chlorine with a small number of atoms of hydrogen (1 to 1, 2 to 1, or some other simple ratio). The constancy of the composition of hydrochloric acid makes the contrary hypothesis (according to which, for example, 976 . . . . atoms of chlorine to 899 . . . . atoms of hydrogen) absolutely improbable.

sible into two parts, that is, it contains at least two atoms.

The same reasoning applies to the hydrogen.

The reaction 2 volumes of hydrogen + 1 volume of oxygen = 2 volumes of water-vapour, shows in the same way that the gaseous particle of oxygen is divisible into two parts, *i.e.* contains two atoms. The study of ammonia leads us to the same conclusion for nitrogen. Hence we write  $H_2$ ,  $Cl_2$ ,  $O_2$ ,  $N_2$ , to denote the single individual particles of these gases. These single individual particles correspond to what we now actually term *gaseous molecules*.

So many excellent arguments have been brought forward in favour of *Avogadro's* hypothesis that it becomes almost as true as a well-ascertained fact.

All gases behave in the same way when compressed or expanded, a fact which indicates a great similarity, or even an identity, of physical structure, and finds its simplest explanation in the admission that in equal volumes of all gases there is the same number of molecules.

Besides, if chemical phenomena had not called for *Avogadro's* hypothesis, the kinetic theory of gases would inevitably have led to it (*Clausius, Maxwell*).

As a third proof it may be added, that all chemical theories which have been based on this hypothesis have introduced simplicity and harmony into the science. It will be profitable now to give an outline of these theories.

## DETERMINATION OF MOLECULAR WEIGHTS

The molecular weight of a gas is proportional to its density.

The lightest substance known, hydrogen, is chosen as standard of comparison. As we denote the atomic weight of hydrogen by 1, the molecule of this gas, containing two atoms, will weigh 2.

Knowing the density of any gas with respect to air we get:

$$M : m = D : d$$

$$M : 2 = D : \frac{1}{14.435}$$

$$M = 2D \times 14.435 = D \times 28.87$$

M, molecular weight of the gas  
m, molecular weight of hydrogen

D, density of the gas (with respect to air)

d, density of hydrogen (with respect to air) =  $\frac{1}{14.435}$

*Remark:* If the density of the gas had been taken relatively to hydrogen, then  $d = 1$ , and we should have  $M = 2D$ , that is, the molecular weight of a substance is equal to twice its vapour density relatively to hydrogen (taken as unity).

### *Correction of Molecular Weights*

There must necessarily be a simple relation between the chemical equivalent,<sup>1</sup> the atomic weight and the molecular weight of an element. We can correct a molecular weight experimentally found by comparing it with the chemical equivalent, which is much more accurately known. For example: the density of chlorine is 2.440, which gives 70.44 for the molecular weight. But 1 gram of hydrogen unites with exactly 35.37 grams of chlorine—this latter number is the equivalent of chlorine. As molecular weight of chlorine we adopt that multiple of 35.37 which approximates most closely to 70.44, the experimentally found value, that is,  $2 \times 35.37 = 70.74$ .

### *Molecular Weights of some Elements known in the Gaseous State*

	M	Temperature
Hydrogen . . . . .	2	0°
Nitrogen .. . . .	28.02	0°

<sup>1</sup> In the case of elements of uneven atomicity the equivalent is frequently equal to the atomic weight. For elements of even atomicity it is generally the half of the atomic weight. These relations, however, are not *absolutely* constant. We shall see later what is meant by the atomicity of an element.

*Molecular Weights—continued*

	M	Temperature
Oxygen . . .	31.92	at 0°
Sulphur . . .	63.96	„ 860° and at 1,500°
	255.84	„ 450°
Chlorine . . .	70.74	„ 200°
	[46.50]	„ 1,567°
Cadmium . . .	111.70	„ 1,040°
Phosphorus . . .	123.84	„ 500° and at 1,040°
Bromine . . .	159.52	„ 100°
	less	„ 1,500°
Selenium . . .	158.0	„ 1,420°
Mercury . . .	199.8	„ 424° and at 1,560°
Iodine . . .	253.07	„ 185° „ 500°
	a half less	„ 1,700°
Tellurium . . .	250.0	„ 1,440°
Arsenic . . .	299.6	„ 860°

*Molecular Weights of Compounds*

These are determined in the same way, and are subject to the same corrections as those of the elements. For example:

Hydrochloric acid;  $D = 1.247$ , which gives  $M = 36$   
 Equivalents . . . 1.00 for hydrogen  
                             35.37 for chlorine

Sum . . . 36.37 = corrected molecular weight

Sulphurous anhydride:  $D = 2.247$  which gives  $M = 64.87$ . In 64.87 parts of sulphurous anhydride there are:

32.40 parts of oxygen, therefore 4 equivalents (or 2 atoms) . . . = 31.92  
 32.47 parts of sulphur, therefore 2 equivalents (or 1 atom) . . . = 31.98

Corrected molecular weight . . . 63.90

## DETERMINATION OF ATOMIC WEIGHTS

The atom of an element is the smallest quantity of it which can enter into chemical combination. The atomic weight of an element is deduced from a study of all the volatile compounds into the constitution of which the element can enter.

If, for example, we are concerned with the atomic weight of chlorine, we know the following volatile compounds containing this element:

*Silicon Chloride*.—Molecular weight experimentally found, 169·5; that is, the molecule weighs so many times more than the atom of hydrogen. Analysis shows that in 169·5 parts of silicon chloride there are 28 parts of silicon, and 141·5 parts of chlorine. In the same way we find the following data for some other volatile chlorides:

Silicon chloride . . .	$M = 169\cdot50$	{ 28·00 silicon 141·50 chlorine
Phosphorous chloride . . .	138·00	{ 31·90 phosphorus 106·10 chlorine
Mercuric chloride . . .	270·00	{ 199·76 mercury 70·74 chlorine
Hydrochloric acid gas . . .	36·37	{ 1·00 hydrogen 35·37 chlorine

Besides these we know a large number of other compounds containing chlorine which are volatile. But not one of them contains in its molecule a quantity of chlorine less than 35·37 times the weight of one atom of hydrogen. This number, therefore, represents the atomic weight of chlorine, *i.e.* the relative weight of the smallest possible particle of this element which can exist in any compound.

The atomic weight thus determined may be too large, but it cannot be too small. The probability of its correctness increases as the number of compounds examined from which it is derived increases. The elements of low atomic

weight are also those which most readily form comparatively light and consequently volatile molecules, and it is particularly to them that this method of determining the atomic weight is applicable.

In this manner the atomic weights of the following elements have been derived: Be, B, C, N, O, F, Al, Si, P, S, Cl, Ti, V, Cr, Zn, Ga, Ge, As, Se, Br, Zr, Nb, Mo, Cd, In, Sn, Sb, Te, I, Ta, W, Os, Hg, Tl, Pb, Bi. (In *L. Meyer's 'Modern Theories of Chemistry'* (English translation by *Bedson and Williams*) a list of the principal compounds studied is given.)

*Remark.*—Comparing the atomic weights with the molecular weights (experimental) we see that the molecule of an element often consists of 2 atoms, sometimes of only 1 atom, and occasionally of 4 or even 8 atoms.

Thus we know  $P_4$ ,  $As_4$ ,  $S_2$  and  $S_8$ , Cd and Hg.

#### ABNORMAL VAPOUR DENSITIES

1. *Small deviations.*—Gases do not exactly obey the laws expressed by the general equation; for moderate pressures, however, the deviation is only small.

2. *Too high densities.*—For certain substances the density is too high when determined too near the boiling point. For instance:

Acetic acid at  $250^\circ$ , Density = 2.08 (normal value).

„ „ „  $125^\circ$  „ = 3.20.

3. *Densities considerably too low* are sometimes found, which lead to a molecular weight smaller than that which corresponds to the lowest possible formula (containing no fractions of atoms).

For instance, ammonium chloride. Analysis leads to the formula  $N_nH_{4n}Cl_n$ , and the smallest value of this is  $NH_4Cl$ , which corresponds to a molecular weight 53.38 and a vapour density  $\frac{53.38}{28.87} = 1.85$ . But *Bineau* has found



the vapour density experimentally to be 0.89, which corresponds to the molecular weight 25.69.

In order to bring these facts into harmony with *Avogadro's* hypothesis and with the admitted atomic weights, the supposition has been made that during volatilisation ammonium chloride is split up and the vapour consists of a mixture of molecules of hydrochloric acid and ammonia. With this supposition all difficulties disappear.

We know quite a number of substances which experimentally give too low vapour densities. Amongst these are: ammonium carbamate, phosphorus pentachloride, antimony pentachloride and pentabromide, sulphuric acid, nitrogen peroxide, chloral hydrate, mercurous chloride, &c.

The vapour density of all these substances is irregular because their vaporisation is accompanied by a more or less complete decomposition, which advances as the temperature rises.

*Pebal* has demonstrated (by his classical experiment) that ammonium chloride is actually decomposed on vaporisation, and by means of their different velocities of diffusion through an asbestos plug he was able to prove the presence of the dissociation products.

In the case of phosphorus pentachloride the greenish colour of the vapour indicates the presence of free chlorine. By volatilising this substance at as low a temperature as possible in an atmosphere of phosphorus trichloride, *Cahours* found a normal vapour density, corresponding to the formula  $\text{PCl}_5$ . This formula is further confirmed by the existence of phosphorus pentafluoride  $\text{PF}_5$ , which is volatile without decomposition.

Besides, in almost every case, the experimental vapour density of a dissociable substance does not agree either with the simple formula or with the halved formula, but has an intermediate value, demonstrating the presence of non-dissociated molecules. These have, therefore, a real existence, and if they do not constitute the whole or even

the greater part of the vapour, this is because the dissociation begins even below the boiling point of the substance.

Further, we know more than one substance whose vapour density does not become abnormal until the temperature is considerably above its boiling point. This is the case with the compounds of amylene with hydrochloric acid, hydrobromic acid, and hydriodic acid, and the progress of the dissociation can be followed step by step. The vapour density is at first normal, then becomes intermediate, and finally assumes only one half the normal value, corresponding to an almost complete dissociation of  $C_5H_{11}R$  into  $C_5H_{10}$  and  $HR$ . Similarly in the case of iodine, the molecule  $I_2$  remains undecomposed up to a temperature of  $500^\circ$ . The dissociation then commences, and at about  $1500^\circ$  the vapour consists for the greater part of isolated iodine atoms.

#### SPECIFIC HEAT OF THE ELEMENTS IN THE SOLID STATE

##### *Dulong and Petit's Law*

The application of *Avogadro's* hypothesis has enabled us to ascertain the atomic weights of a certain number of elements, in particular of the comparatively light elements and those of a non-metallic character. But it leaves us in ignorance of the atomic weights of the majority of the heavier metallic elements.

*Dulong and Petit* observed that the specific heat of an element is inversely proportional to its atomic weight, or, in other words, the atomic heat—which is the product of specific heat and atomic weight—has a constant value for all elements.

The application of this law is, however, limited to the solid elements at temperatures sufficiently below their melting points. Then, taking as unit of specific heat the specific heat of liquid water, and as unit of atomic weight

that of hydrogen, the atomic heat of the elements generally lies between the values 5 and 7, and is nearly 6.4.

For example :

For solid bromine at about  $-51^{\circ}\text{C.}$  the specific heat is  $0.0843$  and the atomic weight is known to be  $79.75$ .

Therefore the atomic heat is  $0.0843 \times 79.75 = 6.7$ . In more concrete terms it may be stated that to raise the temperature of one gram-atom ( $79.75$  grms.) of solid bromine through one degree of temperature,  $6.7$  small calories (gram-units of heat) are required.

A large number of other elements, whose atomic weights we already know (Al, P, Si, Ti, Cr, Zn, Ga, Ge, As, Se, Br, Zr, Mo, Cd, In, Sb, Sn, Te, I, W, Os, Hg, Tl, Pb, Bi), have an atomic heat which falls within the above-mentioned limits. The atom of these elements is therefore that quantity of matter to which a constant quantity of heat must be imparted in order to produce the same rise of temperature.

For the numerous elements for which *Avogadro's* hypothesis is *not* available, we take as atomic weight that multiple of the chemical equivalent which best satisfies the condition :

$$\text{Atomic weight} \times \text{specific heat} = 6.4.$$

By this method of investigation, the atomic weights of the following elements have been determined: Li, Na, Mg, K, Ca, Mn, Fe, Co, Ni, Cu, Ru, Rh, Pd, Ag, La, Ce, Ir, Pt, Au, Th, and U.

Certain elements of low atomic weight have atomic heats which are much too small and do not at all agree with *Dulong and Petit's* law. To this class boron and carbon belong. Silicon agrees better, sulphur and phosphorus have almost normal atomic heats. The values for the light metals (Li, Na, K) are absolutely normal.

*Dulong and Petit's* law, like every other physical law, is only applicable within certain limits. It is only true for solids at temperatures sufficiently distant from their

melting points. The case of carbon seems to show that there is also a lower limit of temperature. Indeed, the specific heat of carbon, as well as that of boron and silicon, increases comparatively rapidly as the temperature rises. If the rate of increase, which has been observed between  $0^{\circ}$  and  $200^{\circ}$ , were maintained above this temperature, the atomic heat of carbon would become normal at about  $500^{\circ}$ .

In practice, *Dulong and Petit's* law, which, as we have seen, is applicable to the heavy elements and in general to all metals, is made the basis of determination of atomic weights for those elements where, by reason of the absence of volatile compounds, *Avogadro's* hypothesis is unable to render assistance. For the determination of the atomic weights of the non-metals or of elements of low atomic weight a study is always made of the volatile derivatives.

#### *Molecular Heat (Neumann)*

The atomic heat of the elements is maintained without modification in their compounds. The *molecular heat* of a substance is equal to the sum of the atomic heats of all the atoms contained in the molecule. We thus meet here what is termed an *additive property* of matter. For example :

The molecular heat of lead bromide,  $\text{PbBr}_2$ , found by experiment is . . . . . 19.9.

That found by calculation is  $6.5 + 2 \times 6.7 = 19.9$ .

From the experimentally found molecular heat of lead chloride,  $\text{PbCl}_2$ , the atomic heat of chlorine can be deduced. It is 5.95.

The investigation of molecular heats of compounds has rendered it possible to derive the following atomic heats :

H . . . . .	2.3	C . . . . .	1.8
O . . . . .	4.0	Si . . . . .	4.0
F . . . . .	5.0	P . . . . .	5.4
N . . . . .	5.5	S . . . . .	5.4
B . . . . .	2.7		

## THE CONSTITUTION OF THE MOLECULE

*Valency or Atomicity (Kekulé)*

A knowledge of the *molecular weights* of a large number of substances as well as of the *number and nature of the atoms* contained in the molecule, shows us that there are certain elements which unite with each other only in pairs, and in such a way that one atom of the one element combines with only one atom of the other. The power of attraction of the atoms of these elements does not extend to more than a single other atom. These elements are termed monatomic or *monovalent*.

There are other elements, a single atom of which is capable of uniting with two, three, four, or more monovalent atoms; their power of attraction extends to two, three, or four other atoms, and consequently they are termed divalent, trivalent, or tetravalent elements.

These peculiarities become evident by inspection of the following formulæ, all of which represent volatile compounds:

I.  $\text{HBr}$ ,  $\text{HCl}$ ,  $\text{HI}$ ,  $\text{H}_2$ ,  $\text{Br}_2$ ,  $\text{Cl}_2$ ,  $\text{I}_2$ .

II.  $\text{OH}_2$ ,  $\text{OCl}_2$ ,  $\text{SH}_2$ ,  $\text{SeH}_2$ ,  $\text{TeH}_2$ ,  $\text{HgCl}_2$ ,  $\text{HgI}_2$ .

III.  $\text{BF}_3$ ,  $\text{BCl}_3$ ,  $\text{BBr}_3$ ,  $\text{NH}_3$ ,  $\text{PH}_3$ ,  $\text{PCl}_3$ ,  $\text{AsH}_3$ ,  $\text{AsCl}_3$ ,  $\text{SbCl}_3$ ,  $\text{BiCl}_3$ .

IV.  $\text{CH}_4$ ,  $\text{CCl}_4$ ,  $\text{SiF}_4$ ,  $\text{SiCl}_4$ ,  $\text{TiCl}_4$ ,  $\text{VCl}_4$ ,  $\text{ZrCl}_4$ ,  $\text{SnCl}_4$ .

V.  $\text{NbCl}_5$ ,  $\text{MoCl}_5$ ,  $\text{TaCl}_5$ .

VI.  $\text{WCl}_6$ .

Experiment also shows that in those compounds or elements belonging to any of the groups II. to VI. the monovalent atoms may be replaced by polyvalent atoms or groups of atoms. Thus

II.  $O_2$ ,  $S_2$ , &c. ;  $O''$  or  $S''$  replacing  $H_2$ .

IV.  $COCl_2$ ,  $CO_2$ ,  $CS_2$ , &c. ;  $O''$  or  $S''$  replacing  $Cl_2$  or  $H_2$ .  $HCN$  ;  $N''$  replacing  $H_3$ .

Without trying to explain the cause of this attractive force of the atoms, we may consider the atoms as possessing a number of poles ; and, by the mutual union of these, the atoms become linked together to form molecules or systems in equilibrium, in which all the poles are saturated.

### *Structural Formulae*

Knowing the molecular weight of a compound, the number and nature of the atoms contained in the molecule, as well as the valency of these atoms, it is possible to arrive at the *chemical constitution* of the substance, that is, the manner in which the atoms are joined together.

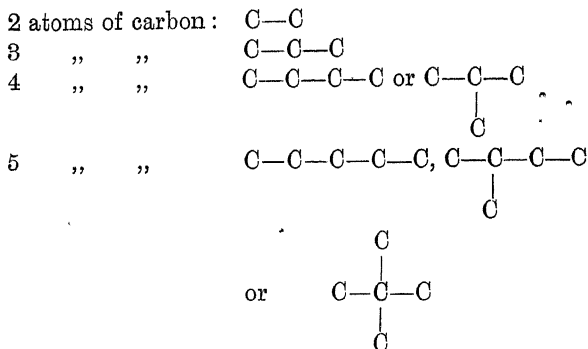
For this purpose it is necessary to form all the possible arrangements of the given atoms, and, if there be more than one arrangement possible, make a choice of the most suitable.

(a) The first part of the problem is purely mathematical and can always be solved. The difficulty increases with the *number*, *valency*, and *variety* of atoms which go to make up the compound. The discovery of all possible arrangements becomes an extremely difficult problem for the numerous compounds of carbon, for which not only the linkage of the carbon atoms (so variable in itself) must be kept in view, but where account must also be taken of the positions on the carbon structure of other atoms of different kinds, which enter into the molecule.

Thus, for the first few members of the hydrocarbon series  $C_nH_{2n+2}$  we have the following possible carbon structures :<sup>1</sup>

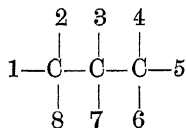
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<sup>1</sup> The free valencies of carbon being saturated by hydrogen, the first combination cited represents  $C_2H_6$ , the second  $C_3H_8$ , the third  $C_4H_{10}$ , and the fourth  $C_5H_{12}$ .



and so on. When the carbon atoms become numerous the number of possible structures becomes very considerable.

If, instead of hydrogen only, other elements of different kinds are united to the carbon nucleus, then the number of possible arrangements increases very rapidly. Thus, for a compound of the type



we can foresee 280 modifications.

b. The second part of the problem to be solved is of a chemical and experimental nature. A large number of molecules, such as  $\text{CH}_4$ ,  $\text{CCl}_4$ ,  $\text{CHCl}_3$ ,  $\text{CH}_3\text{OH}$ ,  $\text{CO}_2$ ,  $\text{COCl}_2$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_2\text{H}_5\text{Cl}$ , and so on, admit of only one interpretation.

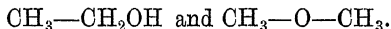
But frequently the molecule admits of several interpretations, and the true constitution, deduced from chemical and physical investigation of the substance, is based on the following two rules :

1. When a reaction takes place between molecules, the atoms or groups of atoms transferred exchange places without the structure of the displaced group of atoms being

disturbed. It is thus possible to deduce the required constitution of a molecule from a knowledge of the constitution of those chains of atoms into which it can be decomposed or from which it can be built up by synthesis.

Examples :

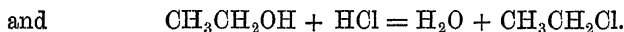
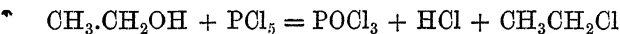
a.  $C_2H_6O$ . Two structures are possible ; viz.



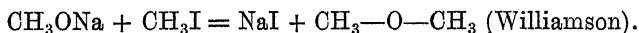
Two isomeric compounds are known : ethyl alcohol and methyl ether.

The alcohol contains a typical hydrogen atom, and, as the formula  $CH_3-CH_2OH$  is the only one which satisfies this condition, it is assigned to the alcohol.

This is confirmed by the fact that ethyl chloride, which can only have the formula  $CH_3CH_2Cl$ , can be obtained from the alcohol by the following reactions :



The methyl ether must, therefore, have the other formula  $CH_3-O-CH_3$ , which suits it perfectly. To begin with, this ether has no typical hydrogen atom, which fact is expressed by the formula, and further, it can be synthesised from substances which admit of only one formula, as for instance :



b. *Constitution of acetic acid,  $C_2H_4O_2$ .*

We have learned that the constitution of ethyl alcohol is  $CH_3CH_2OH$ , and we know from experiment that by oxidation of it we can replace  $H_2$  by  $O$ , and obtain acetic acid. Now this acid contains a typical hydrogen atom, probably forming part of a hydroxyl group. Indeed, only one of the four hydrogen atoms is replaceable by metals or alcoholic radicals. And furthermore, the group  $(OH)$  can be replaced by  $Cl$  in the following manner :

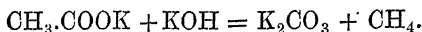




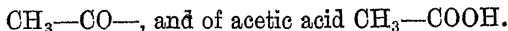
We therefore attribute the formula  $C_2H_3O.OH$  to acetic acid.

But now the question arises, what is the constitution of the radical  $C_2H_3O$ ?

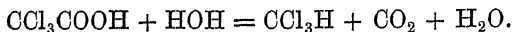
The answer to this was given by *Kekulé*, who observed that the dry distillation of a mixture of potassium acetate and caustic potash yields potassium carbonate and methane. Applying the above principle, we see that in acetic acid the three non-typical hydrogen atoms must be united to one and the same carbon atom:



So that the constitution of the  $C_2H_3O$  radical is



Many reactions confirm this formula, notably the decomposition of trichloroacetic acid with water:



2. Another rule, which may become the principal one in cases where the application of the first is too difficult, is based on the following proposition: *The chemical and physical properties of a substance depend on its molecular structure*; identical or analogous properties proceed from an identical or analogous structure of certain parts of the molecule.

Examples:

(a) *The Alcohols*.—The characteristic properties of alcohols may be fairly represented by those of methyl alcohol (only one formula possible), or by those of ethyl alcohol (formula known). The alcohols are characterised by the formation of alcoholates, simple ethers, saponifiable esters; by certain oxidation products (aldehydes and acids); by the action of phosphorus pentachloride, &c.

Whenever we have to do with an organic substance the empirical formula of which is compatible with the presence of the group  $-CH_2OH$ , we consider it as a

primary alcohol, if the characteristic reactions just mentioned can be realised.

Two substances having the formula  $C_3H_7OH$  are known, and both are of an alcoholic nature. One of them on oxidation gives an aldehyde and an acid, consequently it contains the group  $-CH_2OH$ . It must therefore have the constitution  $CH_3-CH_2-CH_2OH$ , and is normal propyl alcohol.

The isomeric substance yields entirely different oxidation products and no propionic acid. It must necessarily

have the formula 
$$\begin{array}{c} H \\ | \\ CH_3-C-CH_3 \\ | \\ OH \end{array}$$
, the only remaining one

which contains a hydroxyl group. The group  $-CH(OH)-$  thus becomes characteristic of a secondary alcohol. The substance, whose formula is given, is secondary propyl alcohol.

Similar considerations of the alcohols  $C_4H_9OH$  lead us to the characteristic properties and constitution of tertiary alcohols. These contain the group  $-C(OH)-$ . For further details on this subject the reader is referred to treatises on organic chemistry.

(b) *The Fatty Acids*.—Formic acid can only have one formula, and we know the constitution of acetic acid. These two acids contain the group  $-COOH$  which is the characteristic of their properties. Substances which contain this group form salts, saponifiable esters, acid chlorides &c. We know a substance  $C_3H_6O_2$  which is obtained by the oxidation of normal propyl alcohol and which possesses the properties characteristic of the group  $-COOH$ . Hence we conclude that this substance contains this group and has the constitution  $CH_3-CH_2-COOH$  (propionic acid).

It might be interesting here to refer also to the *aromatic compounds*, derived from the nucleus  $C_6H_6$ , all possessed

of certain common properties, but this would lead us too far, and the examples given suffice to show how we apply the principle that *the chemical character of a substance depends on its molecular structure, and that from similar properties a similar structure may be inferred*. It may be added that this principle is a great aid for the elucidation of the chemical constitution of substances.

From the *physical properties* of compounds we may also arrive at certain conclusions with respect to the molecular structure. We shall recur to this subject when dealing with the densities, melting and boiling points, behaviour to polarised light, heat of formation, electric conductivity, and other properties of substances.

*Is valency constant or variable ?<sup>1</sup>*

A new hypothesis is generally brought forward in its simplest and most uncompromising form. For a time it succeeds in explaining the facts then known, and by some clever artifice may even surmount the first difficulties. But sooner or later there comes a time when the exceptions become so numerous that the shortcomings of the theory can no longer be denied. Then the theory must either fall or be modified.

The theory of valency has not escaped this fate. Suggested by the investigation of simple volatile compounds, applied with ingenuity to the interpretation of innumerable carbon derivatives, the hypothesis of invariable valency had victoriously passed through its first trials and promised to be of almost universal application.

Nevertheless, a certain number of substances were known in which the elements of the sulphur group and of the nitrogen group seemed to be endowed with a valency

<sup>1</sup> NOTE BY TRANSLATOR.—In this connection it may be mentioned that *Werner* has proposed a theory which supposes that some of the elements possess, besides their valency, another attractive power which he terms *co-ordination*. The theory was proposed in order to explain some of the metal-amines, and might also be extended to explain water of crystallisation.

higher than that which they usually possessed, namely 2 and 3 respectively.

I may cite here as examples :

*Sulphur group.*—Tetra-substituted sulphonium iodides and hydroxides :  $(\text{CH}_3)_3\text{SI}$ ,  $(\text{CH}_3)_3\text{S.OH}$ .

*Nitrogen group.*—The *ammonium* salts. Ammonium behaves exactly like a monovalent metallic radical, resembling sodium and potassium, and can isomorphically replace the alkaline metals. There may even exist an ammonium amalgam (?).

Phosphonium iodide,  $\text{H}_4\text{PI}$ , the organic ammonium and phosphonium salts such as  $(\text{CH}_3)_4\text{NI}$ ,  $(\text{C}_2\text{H}_5)_4\text{N.OH}$ .

Phosphorus pentachloride,  $\text{PCl}_5$ .

In many compounds, therefore, we must assume sulphur to be tetravalent, and nitrogen pentavalent.

But all these substances belong precisely to that class of compounds which are easily dissociated by heat. Their vapour density is abnormal, and corresponds to a mixture of products resulting from the decomposition.

Thus *Kekulé* was able to say: 'We can only deduce the valency of the elements from the examination of the gaseous compounds. Now ammonium salts do not exist in the gaseous state any more than phosphorus pentachloride does. In the gaseous state I only know  $\text{NH}_3$  and  $\text{PCl}_3$ ; nitrogen and phosphorus are thus trivalent. As for the ammonium salts (in the solid state) they are addition compounds:  $\text{NH}_3.\text{HCl}$ ,  $\text{CH}_3.\text{CO}_2\text{H}.\text{NH}_3$ , &c. And in the same way solid phosphorus chloride is a combination of  $\text{PCl}_3$  with  $\text{Cl}_2$ .'

This artifice served the purpose, and for a long time the theory of constant valency was accepted.

But phosphorus pentafluoride exists in the gaseous state as  $\text{PF}_5$ . Phosphorus pentachloride has a normal vapour density under the conditions already mentioned (see page 16). The density of the vapour from ammonium chloride does not correspond exactly with a mixture of  $\text{NH}_3$  and  $\text{HCl}$  molecules, which shows that a certain number of unde-

composed  $\text{NH}_4\text{Cl}$  molecules are mixed with the dissociation products. The conclusion to be drawn from this is that  $\text{PF}_5$ ,  $\text{PCl}_5$ ,  $\text{NH}_4\text{Cl}$ , &c. represent single molecules capable of existence in the gaseous state. Nitrogen and phosphorus are therefore pentavalent. In an analogous manner the existence of trimethyl sulphonium iodide,  $(\text{CH}_3)_3\text{SI}$ , proves that sulphur is tetravalent. In short, the exceptions have become so evident and so numerous that the theory of constant valency has become untenable.

We are thus forced into the dilemma—whether to place only limited confidence in this beautiful theory of constant valency, or to modify the conception and admit a certain variability of valency.

But if we choose this latter alternative are we not going to be led to a deplorable confusion and compromise the study of the chemical constitution of substances? Are we not going to allow the theorist in his study to dispose of atomicity just as he pleases, and assign the most improbable structural formulæ to compounds?

Fortunately, no! for *Mendeléeff* and *Lothar Meyer* have shown by their classifications of the elements that variable valency obeys certain rules and is a periodic function of the atomic weights.

#### MENDELÉEFF'S CLASSIFICATION OF THE ELEMENTS

In the table on page 29 the elements are arranged in the order of their atomic weights. After each seventh element a new horizontal series commences, and by this division of the elements we obtain seven vertical columns which constitute the true natural families.

Each family is divided into two sub-groups, and the most perfect analogy exists between the members of these sub-groups. For example, the second column contains the sub-groups Be, Mg, Zn, Cd, Hg, and Ca, Sr, Ba. The fifth column is subdivided into N, P, As, Sb, Bi on the

MENDELÉEFF'S CLASSIFICATION

Series	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
1	H							
2	Li	Be	B	C	N	O	F	
3	Na	Mg	Al	Si	P	S	Cl	
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe, Co, Ni
5	Rb	Sr	Zn	Ge	As	Se	Br	
6	Ag	Cd	Y	Zr	Nb	Mo	—	Ba, Rh, Pd
7	Cs	Ba	In	Sn	Sb	(Te)	I	
8	—	—	(La)	(Ce)	—	—	—	—
9	—	—	Yb	—	Ta	W	—	Os, Ir, Pt
10	Au	Hg	Tl	Pb	Bi	—	—	
11	—	—	—	Th	—	U	—	

one hand and V, Nb, Ta on the other. A satisfactory explanation of the necessity of this subdivision is found by considering the horizontal series 3-4, 5-6, 7-8, and 9-10 as forming double periods such that the perfect similarity of an element with a previous member of the same vertical column only recurs after an interval of fourteen terms. Between the sections of each of the long periods 3-4, 5-6, and 9-10, we find elements which are very similar and whose atomic weights differ very little from each other. These so-called transition elements are placed in the eighth vertical column.

This classification shows that the differences in the properties of the elements correspond to correlated differences in their atomic weights. The chemical and physical properties of the elements thus appear to be periodic functions of their atomic weights.

But here I only wish to call attention to the manner in which the VARIATIONS OF VALENCY are regulated by this periodic classification.

Deducing the valency of the elements from their hydrogen compounds (or, in the absence of these, from their compounds with chlorine or hydrocarbon radicals), we find that the valency increases progressively from the first to the fourth vertical column, then gradually diminishes to its initial value :

I	II	III	IV	V	VI	VII
	Mg(CH <sub>3</sub> ) <sub>2</sub>	Al(CH <sub>3</sub> ) <sub>3</sub>	CH <sub>4</sub>	NH <sub>3</sub>	OH <sub>2</sub>	FH
				PH <sub>3</sub>	SH <sub>2</sub>	ClH
LiCl	BeCl <sub>2</sub>	BCl <sub>3</sub>	CCl <sub>4</sub>			

The elements of the first four groups do not combine with a greater number of atoms of chlorine (bromine or iodine). But it is different with the three succeeding groups. If we consider those compounds of the elements with chlorine, oxygen, or hydroxyl, which contain the *maximum* number of these atoms or radicals, we find that the valency increases from the first term to the last.

# MENDELÉEFF'S CLASSIFICATION OF ELEMENTS 31

I	II	III	IV	V	VI	VII
LiCl	BeCl <sub>2</sub>	BCl <sub>3</sub>	CCl <sub>4</sub>	PCl <sub>5</sub>	SCl <sub>4</sub> WCl <sub>6</sub>	IBr <sub>5</sub>
Li <sub>2</sub> O	BeO	B <sub>2</sub> O <sub>3</sub>	CO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	SO <sub>2</sub> and SO <sub>3</sub>	I <sub>2</sub> O <sub>7</sub>
NaOH	Mg(OH) <sub>2</sub>	B(OH) <sub>3</sub>	Si(OH) <sub>4</sub>	P(OH) <sub>5</sub>	S(OH) <sub>6</sub>	I(OH) <sub>7</sub>

The hydroxyl compounds enumerated for the elements of the last columns have no real existence; they lose one or more molecules of water in forming the acids of maximum oxidation.<sup>1</sup>

Thus Si(OH)<sub>4</sub>, P(OH)<sub>5</sub>, S(OH)<sub>6</sub>, I(OH)<sub>7</sub>,  
become SiO<sub>3</sub>H<sub>2</sub>, PO<sub>4</sub>H<sub>3</sub>, SO<sub>4</sub>H<sub>2</sub>, IO<sub>4</sub>H.

Collecting the valencies of the groups with respect to hydrogen and with respect to electronegative radicals in a single table, we get the following :

—	I.	II.	III.	IV.	V.	VI.	VII.
Valency with respect to hydrogen . . .	1	2	3	4	3	2	1
Valency with respect to chlorine or oxygen .	1	2	3	4	5 to 3	6 to 2	7 to 1

Mendeléeff's system conveniently expresses the periodic variations of the valency. Elements which belong to the same group have, as a rule, the same valency, and this is constant with respect to hydrogen, and more or less variable with respect to oxygen and the electronegative elements.

<sup>1</sup> The reader may object that we have made use of formulæ for certain substances whose true molecular weight (by the vapour density) we do not know. To this we reply that we can deduce the size of the molecule of the substances in question: firstly, from chemical considerations. For example, sulphuric acid has the formula H<sub>2</sub>SO<sub>4</sub>, because we may replace half of the hydrogen (NaHSO<sub>4</sub>, KHSO<sub>4</sub>) or all of it (Na<sub>2</sub>SO<sub>4</sub>, K<sub>2</sub>SO<sub>4</sub>). If the formula were double or three times H<sub>2</sub>SO<sub>4</sub>, then a fourth or a sixth of the hydrogen would be replaceable, but this is not the case; and secondly, from physico-chemical considerations which we shall go into later (see the chapters on osmotic pressure, cryoscopy, &c.).



## LOTHAR MEYER'S CLASSIFICATION

It has already been mentioned that not only the chemical character but also the *physical properties* of the elements vary periodically with the atomic weights. *L. Meyer* has shown this interdependence most clearly by making use of a conception which we have not yet noticed, namely, the *atomic volume*.

The space occupied by an atom is obviously directly proportional to the atomic weight and inversely proportional to the density of the element considered. The atomic volume is, therefore, obtained by dividing the atomic weight ( $A$ ) by the density ( $d$ ), i.e. it is equal to  $\frac{A}{d}$ . Putting

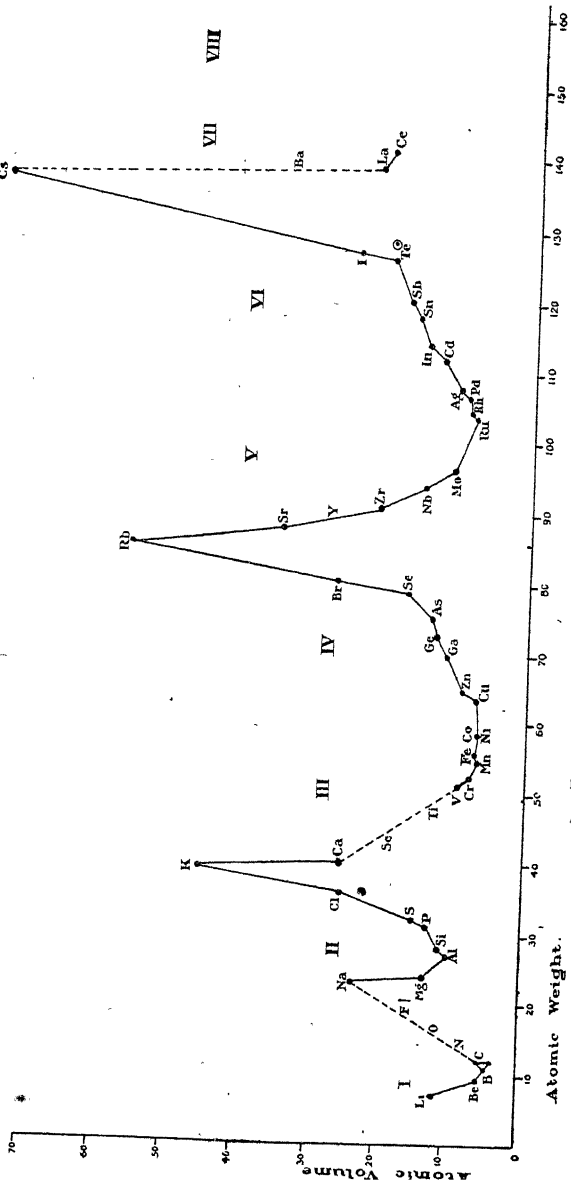
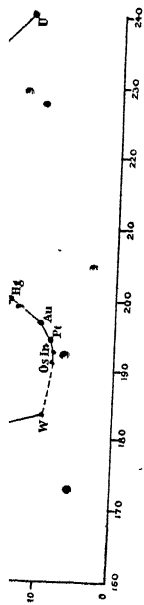
it more concretely, we may say that the ratio  $\frac{A}{d}$  represents the space (in cubic centimetres) occupied by one gram-atom of the element whose atomic weight is  $A$  and whose density is  $d$ .

In order to obtain comparable numbers for the atomic volumes, we must take the density of the elements *in the solid state*.

We obtain a graphic representation of the changes which the atomic volumes undergo as the atomic weight rises, by marking off abscissæ proportional in length to the atomic weights and raising corresponding ordinates proportional in length to the atomic volumes. By joining the co-ordinate points thus obtained we get a curve like that shown in the figure <sup>1</sup> (page 33).

The density *in the solid state* of certain elements such as H, O, N, F, cannot be experimentally determined; but we can foresee by theoretical considerations that this

<sup>1</sup> NOTE BY TRANSLATOR.—*Bekétov* and *Scherbatscheff* (*Bull. Acad. St. Pétersbourg*, 1894 [5], 1) have found that the specific gravity of cesium is 2.366 (and not 1.88 as given by *Settler*): its atomic volume is consequently 56, and not 75.



density would correspond approximately to the place assigned to these elements on the curve.

This curve renders *the periodicity of the atomic volumes* very evident. As in *Mendeleëff's* classification, so also here we find two short or simple periods (1 and 2) followed by long or double periods; 3-4, 5-6, &c. The last periods are still very incomplete.

An important physical property which thus appears as a periodic function of the atomic weight is *the density*; and the same may be said of other properties of the elements.

We shall now examine some of these:

1. THE FUSIBILITY OF THE ELEMENTS.—The gaseous and the easily fusible elements are all to be found on the rising branches and at the summits of the curve. The descending branches and the minima of atomic volumes, on the contrary, correspond to the difficultly fusible or refractory elements.

Those elements, therefore, which have a higher atomic volume than that of the preceding element of lower atomic weight are comparatively easily fusible, and elements for which the opposite holds are difficultly fusible. The transition between these two classes is formed by elements of average fusibility.

The *boiling points* vary in the same way as the melting points. The gaseous or easily volatile elements occupy the ascending portions and the summits of the curve.

The general conclusion is that a large atomic volume (compared with the atomic weight) is favourable to fusibility and volatility.

2. METALLIC OR NON-METALLIC CHARACTER.—The two simple periods begin with a series of metallic elements (summits and descending portions of the curve) and finish with a series of electronegative elements.

The following periods are double, and each of them comprises two series of metallic and ductile elements commencing respectively at the summits and the lowest

points of the curve. These two series are separated by two series of electronegative elements: those non-metals on the descending branches are difficultly fusible; those elements of a non-metallic character on the ascending branches, on the contrary, are easily fusible and volatile.

Besides these very important properties a number of others have found their expression in *L. Meyer's* classification. Amongst these are: the co-efficient of expansion by heat, the refractive index, the thermal and electric conductivity, &c.

This subject may now be concluded by a consideration of a general nature. In the neighbourhood of the minima of the curve of atomic volumes the contrast in chemical properties of the elements is but little marked, whilst in the neighbourhood of the summits the contrary is the case, and the passage from the metallic to the non-metallic nature takes place in the most abrupt manner. It would therefore appear that *the accumulation of a large mass of matter in a small space is not conducive to the development of a well-pronounced chemical character.*

## APPENDIX

With regard to the table on page 29 we see that certain of the periods are quite complete, whilst there are some gaps in others. These gaps correspond with elements which are still unknown, and the periodic law permits us to predict not only their existence but also their properties. This was done by Mendeléeff *à propos* of three elements which he termed eka-boron, eka-aluminium, and eka-silicon, which have since been discovered by *Nilson*, *Lecoq de Boisbaudran*, and *Winkler*, and are now known as scandium, gallium, and germanium.

Such a confirmation certainly tends to show that this periodic classification is an expression of a natural law. It

is, however, no less true that some of the groups in this table have a certain artificiality about them. The strange positions of copper and of gold in the first vertical column and of thallium in the third are self-evident. And the positions of chromium in the sulphur group and manganese in the chlorine group can hardly be justified by the analogous composition and isomorphism of certain of their salts (chromates and sulphates, permanganates and perchlorates).

Tellurium falls into its proper place if we assume that its atomic weight is 125; but the latest determination of this points to the value 127.6, which places tellurium after iodine (126.5) in the table—a position extremely difficult to explain. Again, the atomic weights of some other elements—particularly beryllium, lanthanum, and cerium—are more or less doubtful, and their position in *Mendeleëff's* table is a much-discussed question. Lastly, it is to be noted that there are no missing members of the first three periods, and the positions of argon<sup>1</sup> (atomic weight 40?) and of helium (atomic weight 4?) are very problematic.

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<sup>1</sup> As well as metargon, krypton, and neon.

NOTE BY TRANSLATOR.—In a paper read before the Royal Society (June 1898) *Crookes* proposes an arrangement of the elements on a descending figure-of-eight spiral. In this arrangement the elements helium, neon, argon, and krypton are placed at the points where 'the lemniscate track crosses the neutral line.'

## SECOND PART

### GASEOUS LIQUID AND SOLID STATES OF MATTER

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#### I. THE GASEOUS STATE

##### *Molecular Volume*

In the gaseous state the molecular volume is a *colligative property*, that is to say, a property which belongs to the whole of the molecule.

One gram-molecule of any gas, measured under normal conditions of temperature and pressure (0°C. and 760 m.m.), invariably occupies a volume of 22380 cubic centimetres.

In fact, for a gas with molecular weight  $M$ , the density with reference to hydrogen is :

$$\frac{M}{2}$$

and with reference to air :

$$\frac{M}{2 \times 14.435} ;$$

consequently the weight of one cubic centimetre is :

$$\frac{0.00129 M}{2 \times 14.435}$$

and the volume occupied by  $M$  grams (or one gram-molecule) will be :

$$\frac{M \times 2 \times 14.435}{M \times 0.00129} = 22380 \text{ cubic centimetres.}$$

Let us now apply the general equation of a gas to the gram-molecule and see what value the *constant*  $R$  will assume. We have already put this equation in the form :

$$pv = \frac{p_0 v_0}{273} T \text{ or } pv = RT.$$

Therefore  $R$  represents  $\frac{p_0 v_0}{273}$ .

For one gram-molecule of a gas :

$v_0 = 22380$  cubic centimetres at  $0^\circ$  and under the pressure  $p_0$ .

$p_0 = 760$  millimetres of mercury =  $1033$  grams pressure per square centimetre of surface.

Therefore

$$R = \frac{22380 \times 1033}{273} = 84685.^1$$

In order to arrive at this value for  $R$ , the volume  $v_0$  must be measured in cubic centimetres, and the pressure  $p_0$  in grams per square centimetre of surface.

### *Specific Heat of Gases*

The determination of the specific heat of gases is almost always made *under constant pressure*.

It is extremely difficult to experimentally determine the *specific heat under constant volume*. However, the ratio between the two specific heats has been determined for different gases (*Clement and Desormes's method, Laplace's method*).

For atmospheric air the ratio <sup>2</sup> is  $1.405$ , and *Mayer* has been able to deduce the mechanical equivalent of heat from this.

<sup>1</sup> The number  $84685$  is very often made use of in physico-chemical calculations. It sometimes has an abstract signification; but more often it has a concrete meaning, and represents centimetre-grams of work or an equivalent quantity of some other form of energy (heat, electricity, &c.).

<sup>2</sup> This means that for air the ratio

$$\frac{\text{Specific heat (constant pressure)}}{\text{Specific heat (constant volume)}} = 1.405.$$

For oxygen the ratio is  $1.404$ , for nitrogen  $1.410$ , for ammonia  $1.30$ ,

We shall follow the reverse course, and from the mechanical equivalent of heat deduce the difference which *must* exist between the specific heats of gases under constant volume and under constant pressure.

Let us consider a *gram-molecule of any gas*. If this be heated through one degree under constant pressure, it will expand by  $\frac{1}{273}$  of its volume at  $0^\circ$ , that is, its volume increases by  $\frac{22380}{273} = 81.98$  c.c.

This expansion corresponds to a certain amount of external work: the atmospheric pressure (1,033 grams per square c.m.) has to be repulsed through a distance of 81.98 centimetres.

This work is 84,685 gram-centimetres, and, since the mechanical equivalent of heat is 42,700 gram-centimetres per calorie, it is nearly equal to two small calories.

If the gas be heated *under constant volume* no external work would require to be done, and the quantity of heat which would be imparted to one gram-molecule of the gas would be less by two calories than in the previous case.

Hence, the molecular heat of a gas (specific heat  $\times$  molecular weight) is greater by two calories under constant pressure than under constant volume. The following table gives a few molecular heats:

	Under constant pressure	Under constant volume
$O_2$ . . . . .	6.96	4.96 calories
$N_2$ . . . . .	6.82	4.82 "
$H_2$ . . . . .	6.82	4.82 "
CO . . . . .	6.86	4.86 "
HCl . . . . .	6.76	4.76 "
$SO_2$ . . . . .	9.82	7.82 "
$CHCl_3$ . . . . .	18.55	16.55 "

for chloroform 1.20, and for ethyl ether 1.029. It is evident that as the molecule becomes more complicated the ratio of the specific heats diminishes.

The maximum ratio 1.666 is only realised in those cases where the molecule consists of a single atom, such as mercury and argon.



*The Kinetic Theory*

We must not neglect at this point to give a short survey of what has been termed the Kinetic Theory of the gaseous state.

The apparent volume of a gaseous mass is only filled to a very small extent by material molecules. These molecules are not in a state of rest, but move about in straight lines. They move through space with a very great velocity until they meet the wall of a vessel or another molecule; then the original direction of motion and the velocity are altered, in conformity with the laws of impact of elastic bodies. These collisions are so very frequent that the path of the molecule is zig-zag and made up of very short straight lines. The kinetic energy  $\frac{mv^2}{2}$  is not absolutely the same for each molecule

of the same gaseous mass, because the velocity  $v$  is more or less variable. But for the necessities of the theory and for calculations, we assume that all the molecules of the same gaseous mass have *the same average kinetic energy*.

It is in virtue of this kinetic energy of the molecules that a gas tends to expand and occupy any space, however large; and the impacts of the molecules against the walls of the enclosing vessel constitute the gaseous pressure. It can be shown that this pressure is proportional to the number of molecules contained in unit volume of the gas, and to the kinetic energy of the molecules:

$$P V = \frac{2}{3} n \frac{m v^2}{2}$$

If, at constant temperature, we change the volume of a gaseous mass, it follows that the number of molecules contained in unit volume is changed, and consequently

---

$P$  denotes the pressure and  $V$  the volume of the gas,  $n$  expresses the number of molecules,  $m$  the mass, and  $v$  the average velocity of a molecule.

also the pressure. This number, and this pressure, will evidently be inversely proportional to the total volume occupied by the gas, and thus *Boyle's Law* is explained.

If, at constant volume, we change the temperature of a gaseous mass, then we alter the second factor of the pressure, namely the velocity (and consequently the kinetic energy) of the molecules. Since the pressure is proportional to the absolute temperature (*Gay-Lussac's* or *Dalton's Law*), we are forced to assume that the kinetic energy of the molecules is also proportional to the absolute temperature.

If now we bring together two (or several) different gases at the same temperature and under the same pressure, then the equilibrium of temperature is maintained indefinitely,<sup>1</sup> that is to say, no exchange of energy takes place between the gases, consequently their molecules have the same kinetic energy.

But the two (or several) gases were taken not only at the same temperature but also under the same pressure. Now we have just seen that one of the two factors of the pressure, namely, the kinetic energy of the molecules, is the same for each of the gases. The equality must also exist for the other factor, that is, for the number of molecules contained in unit volume. Thus the necessity of *Avogadro's Hypothesis* is shown by the kinetic theory.

After this summary we may make an interesting comparison. We have seen that the gaseous molecule is that material particle which, at the same temperature, possesses the same kinetic energy for all gases, and whose temperature it is necessary to raise by the same amount to bring about the same increase in kinetic energy whatever be the nature of the gas. In an analogous manner we have found that the atom of any element in the solid state is a material particle to which it is necessary to communicate a constant quantity of heat in order to raise its temperature by one degree (*Dulong and Petit's Law*).

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<sup>1</sup> Provided that no chemical action takes place.

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<sup>1</sup> Provided that no chemical action takes place.

# THE TRANSITION FROM THE GASEOUS TO THE LIQUID STATE

## Compression of Gases

We have already remarked that gases do not obey *Boyle's Law* exactly. In Fig. 3 the pressures are marked as abscissæ (from 0 to 320 atmospheres), and the products of pressures into their corresponding volumes,  $p v$ , as ordinates.

At constant temperature, the line joining the ends of the ordinates ought to be straight and parallel to the axis of abscissæ. This would be the case for a perfect gas, if Boyle's law were absolutely true.

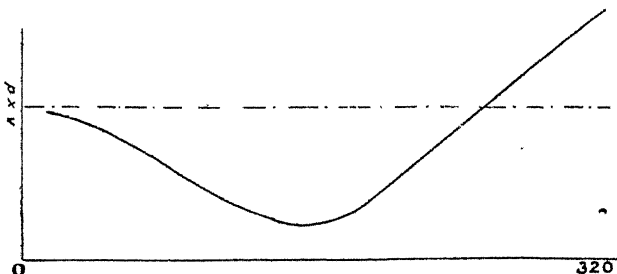


FIG. 3

But, in reality, the isothermal line representing the product  $p v$  is a curve similar to the one shown in the figure. For the lower pressures, up to 40 or even 100 atmospheres, the gaseous mass is generally more compressible than *Boyle's law* requires; the product  $p v$  diminishes as the pressure increases. At a certain point the gas behaves according to the law, but when the pressure is still further increased the compression again becomes abnormal, but in the opposite sense; the volume does not diminish as rapidly as the pressure increases, and the product  $p v$  rises very quickly. This phenomenon has been observed for a large number of gases at pressures

rying from 1 to 320 atmospheres. In *Ostwald's* book,<sup>1</sup> *ragat's* results for the gases, nitrogen, carbon dioxide, methane, and ethylene are graphically represented. In the case of hydrogen we only know the rising part of the curve; from the first, hydrogen is too little compressible. *gnault* has termed it a 'more than perfect gas' ('gaz plus que parfait').

### *Liquefaction of Gases, The Critical State*

When a gas is submitted to an increasing pressure at constant temperature (that is, the operation must be so carried out that this condition is fulfilled), we can observe two different cases :

1. Either, the gas diminishes in volume, at first more rapidly than *Boyle's* law demands, then regularly (the product  $p v$  remaining almost constant), and finally the volume diminishes more and more slowly. The gas then behaves almost like a liquid, and the product  $p v$  rises very rapidly.

Gases of this class have for a long time been considered *permanent*, or non-liquefiable.

2. Or, the gas diminishes in volume more rapidly than *Boyle's* law requires (the product  $p v$  decreases) and when the pressure has attained a certain value, the compressed matter is no longer homogeneous, but separates into two layers, one gaseous and the other liquid. A further decrease of volume does not correspond to a further increase of pressure, but simply to an increase of the liquid layer at the expense of the gaseous layer. A moment arrives when the gas has disappeared, and the whole available space is occupied by liquid; from that moment the laws of the compression of liquids become applicable—even a very large increase of pressure produces only a very small diminution of volume, that is, the product  $p v$  increases almost proportionately with the pressure.

This is the way in which *liquefiable* gases behave.

All gases are liquefiable, but not all at the ordinary temperature nor even at  $0^{\circ}\text{C}$ . Hydrogen and some other gases ( $\text{O}_2$ ,  $\text{N}_2$ ,  $\text{CO}$ ,  $\text{CH}_4$ ,  $\text{NO}$ ) were for a long time considered as permanent—it was found to be impossible to condense them even with extremely high pressures.

The explanation of these phenomena, already foreseen by *Cagniard de la Tour*, was given by *Andrews* in 1869. For every gas there exists a *critical temperature*, above which liquefaction is impossible, and at which liquefaction takes place under the influence of a certain definite pressure and *without change of volume*.

We find here a transition—a kind of confusion—from the gaseous to the liquid state; and we can see the possibility of passing from the one state to the other without the occurrence of any discontinuity in the condition of the substance, that is, without any separation into two layers.

(a) Starting with a gas, we can bring this transition about as follows: Heat the gas to a temperature higher than its critical temperature, then compress it to a pressure higher than its critical pressure, and after that cool it to the critical temperature. Then liquefaction takes place without the formation of two layers, the liquid formed occupies the *whole* space previously filled by the gas.

(b) Starting with a liquid, we first submit it to a pressure higher than the critical pressure, then raise its temperature above the critical temperature. There will be no separation into two layers, but the whole of the substance will assume the gaseous condition. Finally the gas is allowed to expand (furnishing the necessary heat, so that no partial condensation occurs), and the end in view is realised, namely, an absolutely gradual passage from the liquid to the gaseous state without any discontinuity in the homogeneous condition of the substance.

*Experimental Work.*<sup>1</sup>—Before the publication of

The first liquefaction of a gas (chlorine) was performed by

Andrews's first memoir, attempts had been made to liquefy (and even to solidify) a certain number of gases by simultaneous compression and cooling. *Faraday's* (1823-1845) and *Thilorier's* (1835) work on the condensation of quite a number of substances, such as  $\text{CO}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{HCl}$ ,  $\text{SO}_2$ ,  $\text{NH}_3$ ,  $\text{Cl}_2$ , &c., is noticed in almost all books on chemistry. After the study of the critical state had demonstrated the preponderating influence of cooling, it was seen that to attain success in the liquefaction of gases particular attention must be paid to the temperature. In 1877, *Pictet* succeeded in condensing oxygen by a process which differed from that of Faraday only in the use of a better cooling agent—liquid carbon dioxide boiling in a vacuum ( $-130^\circ$ ). In the same year *Caillietet* made use of the cooling effect which accompanies the sudden expansion of a strongly compressed gas.<sup>1</sup> Operating in a glass tube he was able to show that this cooling was sufficient to partially condense, with formation of a more or less dense cloud, oxygen, nitrogen, methane, and carbonic oxide. In the case of hydrogen he saw only a very slight mist.

• In 1883 *Wroblewsky* and *Olczewsky* liquefied oxygen by compressing it in a glass vessel cooled externally by liquid ethylene boiling in a vacuum ( $-136$  to  $-152^\circ$ ). Nitrogen and carbonic oxide can be liquefied in the same way.

Thanks to the recent work of *Ramsay*, *Dewar*, and *Linde*, the liquefaction of air and of its constituents has almost become an industrial process. We can now succeed in making the mist, which *Caillietet* observed, in a continuous manner, and by the condensation of this we obtain a mass of liquid. To accomplish this process the gas is compressed and at the same time subjected to severe cooling; it is then allowed to escape through a narrow opening into a specially constructed receiver made of badly

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<sup>1</sup> In expanding, the gas must perform a very considerable amount of work. If the phenomenon takes place adiabatically, it can be calculated that a fall of pressure from 300 atmospheres to 1 atmosphere produces a decrease in temperature of more than 200 degrees



conducting material.<sup>1</sup> The conditions of the operation may be so combined that the increase in the cooling, due to the expansion of the gas, brings about a partial condensation. A liquid mass at a very low temperature collects in the receiver and can be preserved for a time (even under the ordinary atmospheric pressure).<sup>2</sup>

Air, oxygen, nitrogen (and argon) have been liquefied in this way in considerable quantities.

More recently, *Dewar*<sup>3</sup> has succeeded in obtaining 50 cubic centimetres of liquid hydrogen at a temperature which is only about thirty degrees from the absolute zero. Into this liquid he immersed a glass tube closed at the lower end, and almost immediately the cooled part of the tube became filled with solidified air.<sup>4</sup> A tube of helium was introduced into the liquid hydrogen and the helium liquefied.

The following table gives numerical data for some gases, relating to the critical state and the boiling point :

<sup>1</sup> This receiver generally consists of a double-walled metallic vessel, with the space between the walls evacuated.

<sup>2</sup> The following briefly indicates how *Linde's* apparatus for the liquefaction of air is used (German Patent, No. 88824, June 1895, Class 12). The process is continuous. Air under the pressure  $p_1$  and at temperature  $t_1$  is compressed ( $p_2, t_2$ ) and at the same time cooled by means of an ordinary refrigerator ( $p_2, t_3$ ). This air is then forced into a very powerful refrigerator, whose temperature becomes lower and lower as the process goes on. This refrigerator consists of two worm-tubes  $\sigma$  and  $s$ , the one wound coaxially outside and close to the other. The compressed air passes through the inner worm  $s$ , and its temperature is reduced to  $t_4$ ; it then passes through a regulating valve to an expansion-receiver. The pressure has now been reduced to  $p_1$  and the temperature is further reduced to  $t_5$ . The air thus cooled now passes through the outer worm  $\sigma$ , and lowers the temperature of the whole refrigerator, and consequently also of the compressed air which enters the inner worm  $s$ . The temperature of this air entering the inner worm is thus progressively diminished, and there comes a time when the expansion (in the receiver) must be accompanied by a partial liquefaction.

<sup>3</sup> *Jour. Chem. Soc.* 73, 528 (1898).

<sup>4</sup> *Dewar* proposes to utilise this for the production of a very perfect vacuum.

	CRITICAL STATE			Boiling point under atmo- spheric pressure	Correspond- ing density
	Temperature <sup>1</sup>	Pressure	Density		
SO <sub>2</sub>	155°	78.9 atmo.			
Cl <sub>2</sub>	140°	93.0 "			
CO <sub>2</sub>	31°	74.6 "			
C <sub>2</sub> H <sub>4</sub>	10°	51.0 "			
NO	— 93°	71.0 "		—153.6°	
CH <sub>4</sub>	— 82°	55.0 "		—164°	
O <sub>2</sub>	—118°	50.0 "	{ 0.60 0.65 }	—181.5°	{ 1.124 1.137 }
CO	—140°	39.0 "		—190°	
N <sub>2</sub>	—146°	33.0 "	0.44	—194°	{ 0.885 0.850 }
H <sub>2</sub>	—234°	15.0 „ abt.		—238°	0.07

The numbers obtained for the last six gases are from researches of *Wroblewsky*, *Olczewsky*, or *Dewar*.

The critical constants are also known for a large number of substances which are liquid at the ordinary temperature. The following are a few of these :

	Temperature	Pressure
C <sub>4</sub> H <sub>10</sub> O (Ether)	190°	36.9 atmospheres
CS <sub>2</sub>	272°	74.7 "
C <sub>2</sub> H <sub>5</sub> OH	234°	62.1 "
C <sub>2</sub> H <sub>5</sub> Cl	183°	52.6 "
C <sub>6</sub> H <sub>6</sub>	281°	49.5 "
CHCl <sub>3</sub>	260°	54.9 "
HCOOC <sub>2</sub> H <sub>5</sub>	230°	48.7 "
CH <sub>3</sub> COOC <sub>2</sub> H <sub>5</sub>	230°	57.6 "
H <sub>2</sub> O	365°	200.0 "

The determination of the CRITICAL TEMPERATURE of a liquid is not a very difficult problem. In a glass tube of 4 to 5 millimetres diameter and the walls of which are from 0.75 to 1 millimetre thick, a certain quantity of the substance is placed. The open end of the tube is drawn out to a capillary tube in such a way as to leave the completed

<sup>1</sup> For the measurement of very low temperatures, see works on physics.

apparatus from 4 to 6 centimetres long.<sup>1</sup> The liquid is then boiled and, while the vapour is still issuing, the capillary tube is sealed.

The tube may be filled to two-thirds with the liquid to be examined, leaving the remaining third filled with the vapour of the substance. When the critical temperature is approached, the meniscus of the liquid should be about the middle of the tube.

To determine the critical temperature, the tube is placed alongside a thermometer in a bath of paraffin or in an air-bath with treble metallic walls, and glass or mica observation-windows. By means of a Bunsen burner the temperature is gradually raised. As the critical point is approached, the meniscus of the liquid is seen to lose its sharpness; at the critical point, the meniscus disappears completely and peculiar iridescent flashes generally become visible in the tube. If the temperature be raised slightly above the critical temperature, there remains only gas in the tube.

If the tube is now allowed to cool, the iridescent flashes again make their appearance at the critical point, and at a certain moment one can distinguish in the lower part of the tube some liquid with a sharply defined meniscus.

A very simple method for the determination of the CRITICAL PRESSURE has been devised by *Altschul* in *Ostwald's* laboratory at Leipsic.

The cylinder *c* is filled with paraffin oil, and by means of the screw *y* the pressure within may be varied. Two capillary copper tubes branch off from this reservoir; one of these communicates with a spring manometer filled with oil, and the other with a strong glass tube about 40 centimetres long and 1 to 2 millimetres internal diameter. In Fig. 4 the tube is shown as containing in its upper part the liquid whose critical pressure is to be

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<sup>1</sup> If the liquid be very volatile it is preferable to construct the apparatus completely, then fill it.

determined. The liquid is separated from the paraffin oil of the reservoir by a column of mercury about 10 centimetres long. The glass tube is fixed with sealing-wax into the metallic junction-piece *p* which is screwed on to the copper tube *t*.

By means of the screw *v* the pressure is raised to a little below the expected critical pressure, and the large glass tube *M*, which has been slipped over the experiment tube, is heated by means of a Bunsen burner. After some time vapour begins to form, and consequently also the remaining liquid is separated from the vapour by a meniscus. The heating is continued and in such a way that the upper part (*x*) of the tube is raised above the critical temperature whilst the lower part (*n*) remains cool. Under

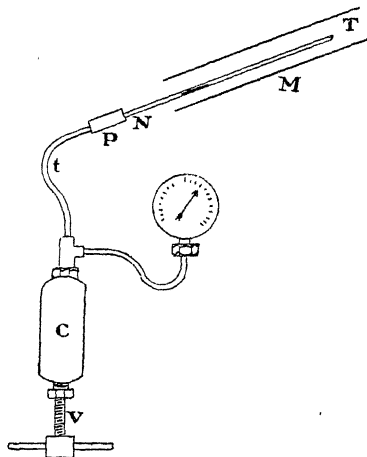


FIG. 4

these conditions there is always a part of the tube where the critical temperature obtains. The screw *v* is then turned so as to gradually increase the pressure. At the moment when the critical pressure is reached the level of the liquid surface will have moved to that part of the tube which is at the critical temperature ; but at this spot the critical conditions will then be completely established ; there will be confusion between the liquid and vapour, and the meniscus will have disappeared. The pressure at which this disappearance takes place is noted as the critical pressure.

There are several indirect methods of ascertaining the

critical constants. I shall refer only to the relation which exists between the critical temperature of a substance and its boiling point measured on the absolute scale.

The critical temperature is equal to twice the boiling point at a greatly reduced pressure (20 millimetres of mercury) or to 1.55 times the boiling point at normal atmospheric pressure.

Thus for chloroform

the boiling point =  $(273 + 61)^\circ$  under normal pressure.

$\therefore$  the critical temperature =  $(273 + 61) \times 1.55 = 518^\circ$

Actual experiment gives the critical temperature as  $533^\circ$  (absolute scale).

## APPENDIX

### VAN DER WAALS'S EQUATION

*Graphical Representation.*—To represent the phenomena studied in the preceding chapter, that is, the transition between the liquid and gaseous states, we can make

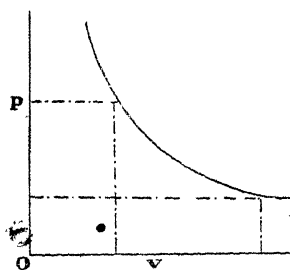


FIG. 5

use of a system of two rectangular co-ordinates and mark off volumes on the abscissæ-axis and pressures as ordinates. For a gaseous mass maintained at constant temperature the correlative values of  $p$  and of  $v$  would determine the successive points of a rectangular hyperbola if Boyle's law were absolutely exact.

Fig. 5 represents such an hyperbola; it is an ideal *isotherm* of the products  $p v$ , and its equation is:  $p v = \text{constant}$ . But in reality the isotherms are quite different from an equilateral hyperbola, as can be seen from fig. 6, which represents a series of *Andrews's*

observations on gaseous and liquefied carbon dioxide. In this figure the pressures are denoted in atmospheres, the zero point of the ordinate starting at 45 atmospheres. The abscissæ-axis is marked off to denote the volumes in thousandths of the normal volume (that is, of the volume occupied by the gas at  $0^{\circ}\text{C}$ ., and under the pressure of one atmosphere). Let us study the *isotherm*  $13.1^{\circ}\text{C}$ . From A to B the pressure increases and the volume diminishes. From B to C liquefaction takes place—the pressure remains

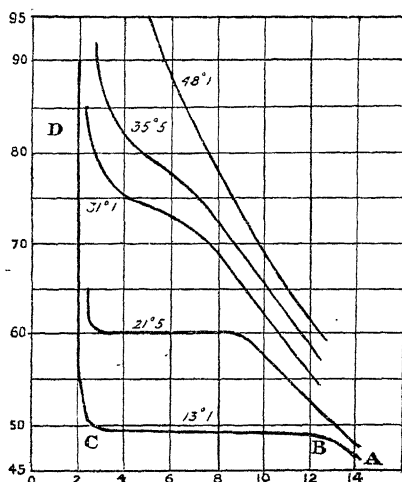


FIG. 6

almost constant, whilst the volume gradually diminishes. This volume corresponds to a non-homogeneous mixture of liquid and gas. After complete liquefaction an increase of pressure produces only a very slight diminution in volume, consequently the product  $pv$  rises very rapidly (curve c D).

At a slightly higher temperature,  $21.5^{\circ}$  for instance, the horizontal line is shorter, that is, the period of liquefaction is reduced. At  $31^{\circ}$  the horizontal line has dis-

appeared, that is, the period of liquefaction is nil, and under a pressure of about 75 atmospheres there is no distinction between the liquid carbon dioxide and the gaseous carbon dioxide—that is, the critical state has been reached: temperature  $31^{\circ}$ , pressure 74.6 atmospheres, volume 0.00573 to 0.00321.

At temperatures higher than  $31^{\circ}$  no liquefaction can take place, and the curve represents entirely the gaseous condition.

*Van der Waals's Equation.*—If the behaviour of a gas is not exactly represented by hyperbola-isotherms, and by the equation  $p v = RT$ , this is probably due to two causes:

1. The apparent volume of a gaseous mass is partly occupied by the material of the molecules. The free space in which the molecular movements can take place is not  $v$  but  $v - b$ .<sup>1</sup>

2. The attraction which exists between the gaseous molecules is very much weakened by the distance across which it acts; however, it is not nil, and for the gaseous state just as for the other states of matter we must assume either a surface tension or a certain degree of cohesion. There exists, therefore, a certain force, caused by the molecular attractions, which, in conjunction with the external pressure, tends to stop the expansion of a gaseous mass and limit its volume. *Van der Waals* assumes that this supplementary force is inversely proportional to the square of the volume occupied by the gas, and its general expression is  $\frac{a}{v^2}$ .<sup>2</sup>

<sup>1</sup> According to *I. Traube*, and in agreement with *Van der Waals's* ideas, the value of  $b$  would correspond to the *vibratory volumes* of the atoms contained in the gaseous molecule, and would generally be to 3.5 times as great as the sum of the material volumes occupied by the atom-nuclei.

<sup>2</sup> It is generally admitted that gases, like liquids, have a certain surface tension; the molecules of the very thin surface layer are attracted by the neighbouring molecules, and there is no counterbalancing attraction from without. Now if we increase the total volume of the gas  $n$  times, then there will be, in a certain definite

If in the general equation for a gas we introduce these corrected values for volume and pressure, we obtain *Van der Waals's* equation :

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT$$

Or arranging the equation in descending values of  $v$  we get :

$$v^3 - \left(b + \frac{RT}{p}\right)v^2 + \frac{a}{p}v - \frac{ab}{p} = 0;$$

that is, it becomes an equation of the third degree, like

$$v^3 - qv^2 + rv - s = 0,$$

and so, according to the values of the variables ( $p$  and  $T$ ), the solution of the equation leads to three real roots for  $v$  or one real root (and two imaginary).

It must be observed that in using *Van der Waals's* equation we do not express, as usual, the pressures in grams per square centimetre of surface and volumes in cubic centimetres;  $p$  and  $a$  are expressed in atmospheres,  $v$  and  $b$  are fractions of the volume occupied by the gas under normal conditions of temperature and pressure. Hence the constant  $R$  has a correlative value. It is hardly

volume of the surface layer,  $n$  times fewer molecules, each of which will be attracted by  $n$  times fewer neighbours. The total attraction will therefore be  $n^2$  times smaller, that is, inversely proportional to the square of the change of volume. This reasoning may seem to be imperfect because it omits entirely the variation of the attraction due to change in the intermolecular distances. One might also say that the expression  $\frac{a}{v^2}$  was justified *a posteriori*, by the consequences of *Van der Waals's* equation, rather than *a priori*, by good scientific reasoning.

The term  $\frac{a}{v^2}$  may attain very high values, exceeding even the external pressure  $p$ . We shall presently see that for carbon dioxide,  $a = 0.00874$ . Now at  $21.5^\circ$  carbon dioxide, liquefied by a pressure of 60 atmospheres, is reduced to about 0.003 of its normal volume. Hence the value of  $\frac{a}{v^2}$  in this case is  $\frac{0.00874}{0.000009} = 971$  atmospheres.



necessary to point out that the values of  $a$  and  $b$  depend on the nature of the gas under examination.

*Application of the Equation.*—In order the better to understand these theories let us take an example, and again we shall choose *Andrews's observations on carbon dioxide*.

It has been found that *Van der Waals's equation* conveniently expresses the behaviour of gaseous carbon dioxide

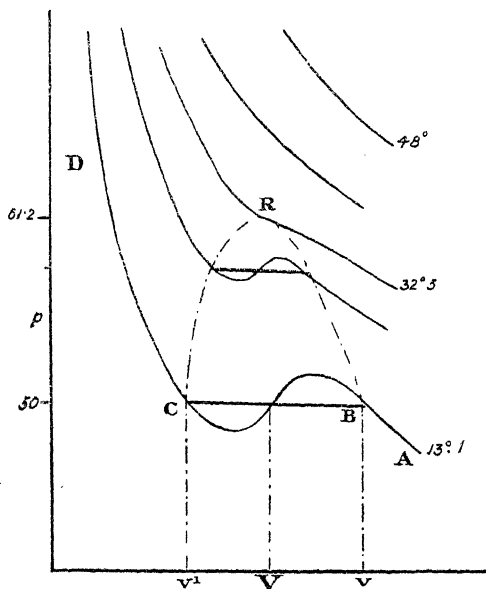


FIG. 7

if we put  $a = 0.00874$  and  $b = 0.0023$ . At  $0^\circ\text{C}$ . and under one atmosphere pressure we should have :

$$(1 + 0.00874) (1 - 0.0023) = R \times 273$$

which gives for  $R$  the value  $\frac{1.00642}{273}$ .

At the temperature  $t^\circ\text{C}$ . the equation will be :

$$\left(p + \frac{0.00874}{v^2}\right) (v - 0.0023) = \frac{1.00642}{273} \times (273 + t).$$

From this equation, calculating the correlative values of  $p$  and  $v$ , we obtain isotherms which fully interpret the results obtained by *Andrews*. At temperatures above  $32.5^\circ$ , each value of  $p$  corresponds to only one value for  $v$  (the equation has only one real root) and the isotherms represent the gaseous state. At temperatures below  $32.5^\circ$  and for certain values of  $p$  the equation yields three real roots, that is, it corresponds to three different volumes. In fig. 7, the isotherm for  $13.1^\circ$  shows that under a pressure of about 50 atmospheres the same mass of carbon dioxide can occupy the volume  $v$  (in the gaseous state), the volume  $v^1$  (after complete liquefaction) and the third volume  $v$ . This last corresponds to an unstable state of the material, for which a diminution in volume would correspond to a diminution of pressure. The volume  $v$  cannot be realised by homogeneous carbon dioxide.

At  $32.5^\circ$  and for a pressure of about 61 atmos., the equation again leads to three real roots, but now they coincide and correspond only to one volume—the critical state has been reached.

\* *Calculation of the Characteristics of the Critical State.*—When the general equation of the third degree (see above) gives three real and equal roots, we have the following relations :

$$3v = q$$

$$3v^2 = r$$

$$v^3 = s$$

Under the same conditions, that is, for a substance taken in its critical state, Van der Waals's equation gives us

$$3v = b + \frac{R T}{p},$$

$$3v^2 = \frac{a}{p},$$

$$v^3 = \frac{a b}{p},$$

and from these three equations we can deduce the characteristics of the critical state,  $v_1$ ,  $p_1$ ,  $T_1$ , expressed in terms of  $a$ ,  $b$ , and  $R$ :

$$\begin{array}{lll} \text{the critical volume . . . .} & v_1 = 3b \\ \text{,, ,, pressure . . . .} & p_1 = \frac{a}{27 b^2} \\ \text{,, ,, temperature . . . .} & T_1 = \frac{8}{27} \cdot \frac{a}{b R}. \end{array}$$

For carbon dioxide, the critical temperature thus calculated ( $32.5^\circ$ ) approximates fairly closely to that experimentally found by *Andrews* ( $31^\circ$ ). For the pressure and volume the agreement is not quite so good ( $61.2$  and  $0.0069$ , instead of  $74.6$  and  $0.00447$  found experimentally).<sup>1</sup>

The constants  $a$  and  $b$  and the critical temperature of other substances have also been established by calculation in quite a satisfactory manner.

*The Theory of the Corresponding States.*—If in *Van der Waals's* equation we put

$$p = \pi p_1, v = \phi v_1 \text{ and } T = \theta T_1,$$

that is to say, if we consider the actual pressure  $p$  as a fraction  $\pi$  of the critical pressure  $p_1$ , and in the same way the volume and temperature as fractions,  $\phi$  and  $\theta$ , of the critical volume and temperature; and if at the same time we express  $a$  and  $b$  in terms of  $p_1$  and  $v_1$ :

$$b = \frac{v_1}{3}, a = 27 p_1 b^2 = 3 p_1 v_1^2:$$

then after some simple transformations we obtain

$$\left( \pi + \frac{3}{\phi^2} \right) (3\phi - 1) = 8\theta.$$

<sup>1</sup> *Van der Waals's* equation gives a very good *qualitative* interpretation of the facts observed by *Andrews*. From the *quantitative* point of view the interpretation is not quite so good. The reader will gain a good idea of this inexactitude by calculating the values of  $p$ , for a given temperature, which correspond to different values of  $v$ , and describing the isotherm thus determined beside the experi-

This equation is extremely interesting, because it now does not contain anything peculiar to one substance, but is applicable to all bodies. It gives rise to the idea that to compare the properties of several substances, liquid or gaseous, it would be rational to take these substances *in corresponding states*, that is, at temperatures  $\theta T_1$ , and under the pressures  $\pi p_1$ , such that  $\theta$  and  $\pi$  have the same value for all the bodies compared. Unfortunately the critical constants are not known for a sufficient number of substances to enable us yet to carry this method very far. We have, however, already seen an application of this principle—the calculation of the critical temperature of a substance in terms of its boiling point (absolute scale).

## II. THE LIQUID STATE

The characteristic of the liquid state is that a given mass of liquid has a definite volume but no definite form.

Liquids are but slightly compressible.

The *expansion by heat* varies according to the nature of the liquid. The behaviour of water on heating is peculiar. From  $0^\circ$  to  $4^\circ\text{C}$ . contraction takes place; from  $4^\circ$  to  $50^\circ\text{C}$ . it expands by about 1 per cent. of its volume at  $0^\circ$ ; from  $50^\circ$  to  $100^\circ\text{C}$ . it expands still further by about 3 per cent. of the same volume.

### *The Boiling Point*

In order that the correct boiling point of a substance may be determined by distillation,<sup>1</sup> the following points must be observed.

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mentally obtained results in fig. 6.—*Clausius* has modified the equation by introducing a third constant. He has thus succeeded in calculating with very close approximation the characteristics of the critical state. Preference, however, has here been given to *Van der Waals's* equation because it is relatively simple, qualitatively satisfactory, and the first proposed.

<sup>1</sup> The operation is carried out in one or other of the apparatus shown in fig. 8, *a* and *b*. The bulb of the flask should be filled to a third or a half with the substance to be distilled. During the course

1. The mercury column of the thermometer must be entirely in the vapour.

2. The barometric pressure must be normal.

3. The operation must be conducted at a moderate rate.

It is easy to fulfil the first of these conditions, especially if a set of short-stem thermometers marking only a limited number of degrees ( $0^{\circ}$  to  $50^{\circ}$ ,  $50^{\circ}$  to  $100^{\circ}$ ,  $100^{\circ}$  to  $150^{\circ}$ , &c.) be used. But when an ordinary  $0^{\circ}$  to  $360^{\circ}\text{C}$ . thermometer is used, it is not easy to have the whole of the mercury column immersed in the vapour if the boiling point of the liquid is fairly high. In this case a correction must be introduced. Let  $\tau$  be the observed boiling point,  $t$  the mean temperature of the projecting part of the column of mercury,  $n$  the length of this column in thermometric degrees, then, since the apparent coefficient of expansion of mercury in glass is 0.000154, it is at once evident that if the whole of the mercury column were surrounded by hot vapour, the  $n$  degrees would be prolonged by  $n(\tau - t) 0.000154$  degrees. The corrected boiling point would, therefore, be  $\tau + n(\tau - t)$

0.000154 degrees. To determine  $t$  a small auxiliary thermometer is attached to the principal thermometer with its bulb just about the middle point of the projecting mercury column.

If the distillation take place at a pressure other than 760 m.m., another correction must be made. If the barometer indicates  $b$  m.m., then the corrected boiling point is obtained by adding to the temperature denoted by

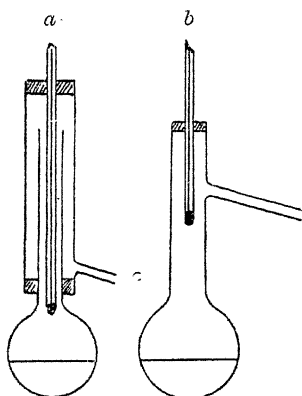


FIG. 8

of the operation the vapour passes through the lateral tube and can be condensed by means of an air or a Liebig condenser and collected in a suitable receiver.

the thermometer,  $0.0375(760 - b)$  degrees. The correction is negative or positive, according as the barometric pressure at the time is higher or lower than normal.

In the case of substances which can only be distilled under diminished pressure, data concerning the boiling point should always be accompanied by information of the pressure at which the distillation was carried out.

### *Observed Regularities*

It has already been pointed out that, according to *L. Meyer*, the volatility of *the elements* is a periodic function of their atomic weights.

*H. Kopp* has proposed the following general law for *organic substances*. For analogous substances a given difference in chemical composition gives rise to a constant difference in the boiling point. The following additions have been made to this law by *L. Meyer* in his 'Modern Theories of Chemistry.'<sup>1</sup>

1. The boiling points of isomeric substances of analogous constitution do not differ much :

*Example*.—Butyl acetate boils at  $124^{\circ}$ ; propyl propionate boils at  $122^{\circ}$ ; ethyl butyrate boils at  $121^{\circ}$ .

2. Isomeric substances of dissimilar constitution have different boiling points; and, for a given difference in the constitution, there is a constant difference in the boiling point.

*Example*.—Propionic acid, on the one hand, boils at  $140^{\circ}$ , methyl acetate and ethyl formate, on the other, boil at  $56^{\circ}$  and  $55^{\circ}$  respectively.

3. Where several substances have an analogous constitution but different molecular weights, there is a constant difference in their boiling points for a given difference in molecular weight.

*Example*.—In the series of the normal fatty acids the

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<sup>1</sup> English translation by Bedson and Williams.

boiling point rises by about  $20^\circ$  for the addition of each  $\text{CH}_2$ .

Formic acid boils at  $99^\circ$

Acetic acid       ,,     $118^\circ$

Propionic acid   ,,     $140^\circ$ , and so on.

This regularity has only been observed for the first six or seven members of the series. It is also to be generally noticed that the change of boiling point brought about by the addition of  $\text{CH}_2$  tends to diminish as the substance becomes richer in carbon.

For the aromatic hydrocarbons  $\text{C}_n\text{H}_{2n-6}$  the introduction of a  $\text{CH}_2$  group into a lateral chain produces a normal rise of about  $20^\circ$  in the boiling point. But if the addition takes place directly on to the benzene nucleus, the boiling point is raised by about  $30^\circ$ .

*Example.*—Benzene boils at  $80.4^\circ$

Toluene       ,,     $110.3^\circ$ .

The three xylenes boil from  $137^\circ$  to  $143^\circ$ .

4. Where the substances differ not only in molecular weight but have also different constitutions, then, for a given difference in these two factors, there is a correlative difference in the boiling points.

*Example.*—An acid generally boils about  $40^\circ$  higher than the alcohol from which it is obtained by oxidation.

Formic acid boils at  $99^\circ$        Acetic acid boils at  $118^\circ$

Methyl alcohol   ,,    $60^\circ$        Ethyl alcohol   ,,    $78^\circ$

Benzoic acid boils at  $250^\circ$

Benzyl alcohol   ,,    $207^\circ$ .

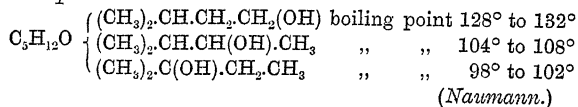
But that is now sufficient for *Kopp's* law as developed by *L. Meyer*. The law is not without exceptions any more than the following rule taken from the works of *Naumann* and *L. Henry*.

5. When we consider isomeric substances derived from the same hydrocarbon by substitution of one or more hydrogen atoms, by certain elements (Cl, Br, I, O), or by

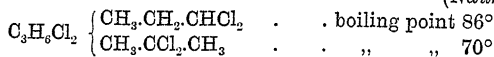
certain radicals (OH, CH<sub>3</sub>, &c.), we generally find that the volatility of the substances is favoured by the two following circumstances :

(a) by the central position in the molecule of the substituting atom or radical.

*Examples.*—



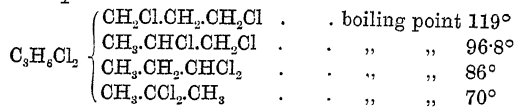
(*Naumann.*)



(*Henry.*)

(β) by the substituting atoms or radicals being close together.

*Example.*—



(*Henry.*)

This regularity applies also to the aromatic series (benzene-derivatives) where the di-substituted *ortho*-derivatives are generally more volatile than the corresponding *para*-derivatives.

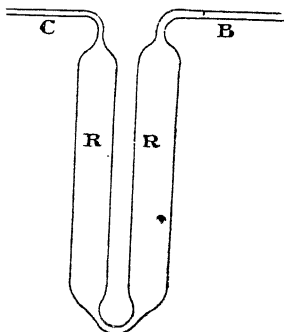


FIG. 9

### *Specific Gravity*

For information concerning aræometers and pycnometers the student is referred to text-books on physics. But here *Sprengel's pycnometer* may be mentioned. The apparatus can easily be made from ordinary glass-tubing

(fig. 9). The reservoir R ends in two horizontal branches, one of which, C, is a fine capillary tube, whilst the other, B,



is only moderately narrow and carries a mark. By means of a platinum wire attached to the bends, the apparatus can be suspended on a balance. The substance whose specific gravity is to be determined is filled into the apparatus by aspiration. The instrument and its contents are then brought to the desired temperature by immersion for a few minutes in a water bath at that temperature. If, after assuming this temperature, the meniscus of the liquid in the branch *b* is not exactly at the mark, it can very easily be adjusted. To remove an excess of the liquid it is only necessary to bring a piece of filter paper in contact with the capillary end *c*; or, if it be necessary to fill a little more liquid into the apparatus, then a glass rod with a drop of the liquid hanging at the end is brought in contact with the end of *c*. The weight *p* of the empty instrument, *p'* of the instrument filled with water<sup>1</sup> at *t*°, and the weight *p''* full of substance at *t*° are then determined. The weight of the substance is then  $m = p'' - p$ , and the weight of an equal volume of water is  $w = p' - p$ . For ordinary determinations the specific gravity or density, *d*, at *t*° is equal to  $\frac{m}{w}$ .

But in scientific work it is usual to take as standard of comparison not water at *t*° but water at its maximum density (at 4°C.). Accuracy to the fourth decimal place can be obtained by reducing the weighings to vacuum. This double correction can be made by means of the formula:

$$d \frac{t^\circ}{4^\circ} = \frac{m}{w} \rho(-\lambda) + \lambda$$

where  $\rho$  denotes the density of water at *t*° and  $\lambda$  the density of the air during the time of the experiment.

$\rho$  can be obtained from chemical tables, and for  $\lambda$  it is generally sufficient to take the average value 0.0012.

The pycnometric method is very exact, but requires considerable time. We can obtain results much more quickly,

<sup>1</sup> It is preferable to take boiled water as free as possible from air.

although less accurately, by making use of *Mohr's* or *Westphal's balance*. This instrument is shown in fig. 10. The part of the beam to the right is graduated and carries at its extremity a link from which a thermometer-sinker is suspended. When the sinker is attached the balance is in equilibrium. If now the sinker be immersed in distilled water at  $15^{\circ}\text{C}.$ , the equilibrium is, of course, disturbed, and to re-establish the equilibrium it is necessary to hang a

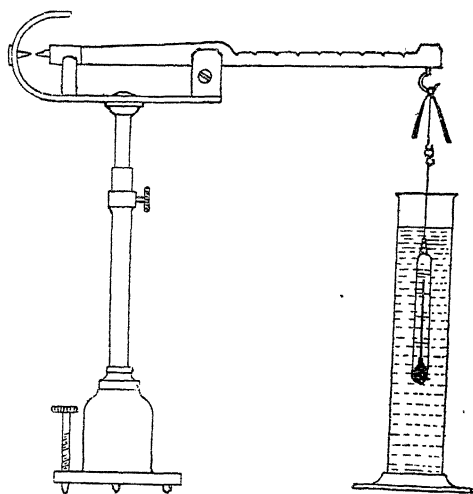


FIG. 10

weight on to the link equal to the weight of the water displaced by the sinker. This weight is the *unit* weight of the system.

A series of weights in the form of riders of the respective values 1.0, 0.1, 0.01, may be placed on the graduated part of the beam.

Suppose the sinker to be immersed in a liquid denser than water, then the following arrangement of the riders (for example) would be necessary: (1) the weight 1, suspended on the link — value = 1.000; and (2) other weights distributed at different points of the beam:

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$$d \frac{t^\circ}{4^\circ} = \frac{m}{w} Q(-\lambda) + \lambda$$

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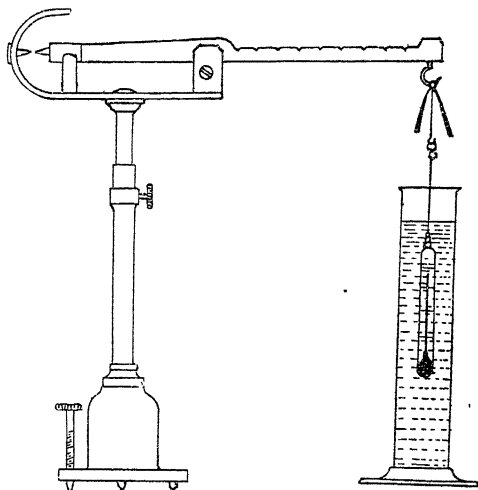


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The rider	1.0	at division	8	=	0.8
"	"	0.1	"	"	6 = 0.06
"	"	0.01	"	"	3.7 = 0.0037
Total	.	.	.	1 +	0.8637

The volume of liquid displaced by the sinker is the same as in the case of water, since the operation is carried out at the same temperature (15°C.).

The water displaced weighed 1.0 and the liquid displaced weighs 1.8637; this number, therefore, expresses the specific gravity of the liquid.

If the liquid is lighter than water, then the weight 1.0 would not require to be suspended on the link, but no other change in the method would be necessary.

**THE MOLECULAR VOLUME.**—The volume of a gram-molecule of water (at 4°C.) is 18 cubic centimetres. The volume of a gram-molecule of any other substance of molecular weight  $M$  would be  $M$  cubic centimetres if the substance had the same density as water. But the density being  $d$ , the molecular volume becomes  $\frac{M}{d}$ .

The molecular volume of a substance is proportional directly to its molecular weight and inversely to its density.

In order to discover any regularities which the molecular volumes of liquids might present it is essential, according to *H. Kopp*, to take the different substances in comparable states. *Kopp* selected as the temperature of comparison the boiling points of the liquids, *i.e.* the temperature at which their vapour tension is equal to one atmosphere.

The determination of the density of a liquid at its boiling point can be made by means of the direct method of *Ramsay* and *Lothar Meyer*. *Kopp* proceeded by indirect means; he took the density of the liquid at several different temperatures and thus found the cubical coefficient of expansion, and from it he calculated the density at the boiling point.

Comparison of the results obtained led to the establish-

ment of a system of which the following are the chief points:

1. Isomeric substances have the same molecular volumes.

2. Equal differences in composition correspond to equal differences in molecular volume.

The consequence of this is that the volume of a molecule is composed *additively* of the volumes of the atoms which it contains.

In order to determine *atomic volumes* *H. Kopp* ascertained that in homologous series the addition of the group  $\text{CH}_2$  increases the molecular volume by 22 units.

<i>Example.</i> —	Molecular volume
Formic acid . . . . .	42
Acetic „ . . . . .	64
Propionic „ . . . . .	86
Butyric „ . . . . .	108

He also found that the substitution of two atoms of hydrogen for one atom of carbon does not change the molecular volume.

<i>Example.</i> —	Molecular volume
Cymol $\text{C}_{10}\text{H}_{14}$ . . . . .	187
Octane $\text{C}_8\text{H}_{18}$ . . . . .	187

From these two experimentally ascertained facts, he was led to the conclusion:

$$\text{CH}_2 = 22, \text{C} = 11, \text{H} = 5.5.$$

By investigating such a substance as  $\text{C}_4\text{H}_9\text{Cl}$  and subtracting from its molecular volume the volume of four carbon atoms and nine hydrogen atoms, *Kopp* was able to find the atomic volume of chlorine.

By further application of this empirical principle, *Kopp* has determined the atomic volumes of a number of elements (O, Cl, Br, I, S, N, &c.), and has confirmed the general *additive character* of the molecular volume. He also recognised the necessity of taking into account certain *constitutional influences*. For instance, oxygen in the

group OH (extra-radical oxygen) has the atomic volume 7·8, whilst oxygen which is doubly linked with carbon (intra-radical oxygen) has a greater atomic volume value, namely, 12·2. For sulphur and nitrogen there are similar variations.

Amongst the most interesting deductions from these observations are the following: (1.) For unsaturated compounds the calculated molecular volume is only equal to the experimental after the addition of 4·4 units for each double bond which occurs in the molecule. (2.) The hexahydro- derivatives of benzene and its homologues have a smaller molecular volume than the isomeric olefines of the fatty series. The formation of the aromatic ring is therefore accompanied by a contraction of the molecule.

The large number of experimental facts which have been ascertained by *Kopp*, *Lossen*, *R. Schiff*, *Schroeder*, and others, have shown, however, that the system of calculation, the basis of which has just been given, is not capable of general application. The atomic volume of all the elements, hydrogen included, is more or less variable. The atomic volume of oxygen may even become negative:

	Molecular volume
Propyl alcohol, $C_3H_8O$ . . . . .	73·4
Propylene glycol, $C_3H_8O_2$ . . . . .	72·1
Atomic volume of O . . . . .	<hr/> -1·3

In an attempt to account for these irregularities, *I. Traube* finds the causes of failure of *Kopp's* system in the following considerations:

(1.) A large number of substances form in the liquid state polymerised molecules which are  $n$  times greater than the gaseous molecules. The formation of these molecular aggregates being very probably accompanied by a contraction, it would seem evident *a priori* that no regularity found with such substances would hold good with non-associated substances; and *vice versa*.

*Ramsay and Shields*<sup>1</sup> have shown by their capillary-metric investigations that the associating tendency belongs particularly to comparatively light molecules containing hydroxyl groups. Water, methyl alcohol, ethyl alcohol, glycol, glycerine, formic acid, &c., belong to this class of compounds. The molecules of most of the organic liquids which do not contain a hydroxyl group (hydrocarbons, ethers, &c.), are simple and non-associated, and this is the more true if the lower members of the homologous series are left out of consideration.

(2.) In the gaseous condition the actual space materially filled by the molecule (*b* in *Van der Waals's* equation) is so small, compared with the total volume of the gas, as to be negligible. This latter volume is of a colligative nature and satisfies *Avogadro's* hypothesis. We may well ask ourselves whether the molecule of a liquid has not, like the gaseous molecule, an additional space, unoccupied by matter, at its disposal; *i.e.* whether the liquid molecule does not possess a colligative *co-volume*. Indeed, it appears that there is such a *co-volume*, to which *Avogadro's* hypothesis applies; that is to say, for all liquid particles (simple or polymerised) taken at the same temperature and under the same pressure, the *co-volume* is the same.

*I. Traube*, by studying a number of series of non-associated substances (hydrocarbons, ethers), has found that the molecular volume  $\frac{M}{d}$  is composed of an additive part, the sum of the atomic volumes, and of a *co-volume*. This latter has the value  $24.5 (1 + \alpha t)$  cubic centimetres, the coefficient  $\alpha$  being the same as the coefficient of expansion for gases.<sup>2</sup> At the temperature of 15° the *co-volume* amounts to 25.9 c.c.

<sup>1</sup> *Journ. Chem. Soc.* 63, 1191, and *Zeitschrift für phys. Chem.*, 12, 433.

<sup>2</sup> It has been found that the *co-volume* is generally the same for the solid and the liquid state. When a compound is gasified the *co-volume* suffers an increase, which becomes zero at the critical state (*i.e.* at the critical temperature and under the critical pressure).



The atomic volumes adopted in this new system are :

—	At 15°C.	Remarks
CH <sub>2</sub> . . .	16.1	15.97 at 0°, 17.13 at 100°C.
C . . .	9.9	
H . . .	3.1	
O intra-radical .	5.5	Oxygen doubly linked to carbon, either to one carbon atom or to two different carbon atoms.
O extra-radical .	2.3	This value becomes 0.4 when OH is fixed on to a carbon atom to which a doubly linked oxygen atom is attached, or when the neighbouring carbon atom has a hydroxyl attached to it.

From the study of a large number of series of organic liquids of very different natures (chlorides, bromides, iodides, nitriles, ethers, acid chlorides, anhydrides, sulphides, amines, &c.) *Traube* has deduced the following atomic volumes more or less approximately :

S (sulphydryl, sulphonyl) . . .	15.5	N (primary amines) . . .	1.5
S (united to oxygen) 10 to 11.5		N pentavalent . . .	10.7
Cl, Cy . . .	13.2	N (nitro) . . .	8.5 to 10.7
Br . . .	17.7	P trivalent . . .	17.0
I . . .	21.4	P pentavalent . . .	28.5

The following numbers must be deducted to allow for ring formation and double and treble linking :

For a hexamethylene ring . . .	— 8.1
For a double linkage . . .	— 1.7
For a treble linkage . . .	— 3.4
For a benzene ring . . .	— 13.2 = (— 8.1 + (3 × — 1.7) ).

By means of these values (more or less corrected if the density of the substance has been taken at a temperature

The constant  $\alpha$  having the same value ( $\frac{1}{273}$ ) as for gases, we see that the idea of absolute temperature can be deduced from the properties of liquids and solids as well as from those of gases.

differing much from  $15^{\circ}\text{C}.$ ), we can calculate the molecular volume  $\frac{M}{d}$  of a substance by simply adding together the atomic volumes and the co-volume. It is, of course, necessary to know the molecular weight of the substance and its constitution and make the necessary deductions, if any, for double linkage and so on. Generally the number thus obtained does not differ much from that found by experiment, *provided the following conditions be satisfied*:

(1.) The molecular weight taken must be exact. Suppose for a moment that this has erroneously been taken twice too large, then the molecular volume would be  $\frac{2M}{d}$  ( $M$  being the correct molecular weight).

To find the same value by the theoretical method, we should have to take the sum :

$$2 \Sigma \text{ atomic volumes} + \text{twice } 25.9.$$

The error in the molecular weight would lead us to the sum :

$$2 \Sigma \text{ atomic volumes} + \text{once } 25.9,$$

*i.e.* the theoretical number for the molecular volume would be too small by one co-volume.

These considerations show, on the one hand, that the co-volume has the value assigned by *Traube* and, on the other hand, that the experimental determination of the molecular volume  $\frac{M}{d}$  of a substance gives us a means of checking the exactitude of the molecular weight provisionally accepted. The value of  $M$  must satisfy the equation,

$$\frac{M}{d} = \Sigma \text{ atomic volumes} + 25.9.$$

(2.) The substance must not be *associated*, otherwise the normal co-volume would only have to be counted once

for each polymerised particle (consisting of  $n$  times  $M$ ), and we should then have

$$\frac{M}{d} = \Sigma \text{ atomic volumes} + \frac{25.9}{n}.$$

*The Association Factor.*—When the molecular weight of a substance is known, the experimental determination of the co-volume  $\left(\frac{M}{d} - \Sigma \text{ atomic volumes}\right)$  may be used as a means of ascertaining the degree of association.

If at  $15^\circ$  the co-volume is  $\frac{25.9}{x}$ , then the liquid is composed partially or wholly of polymolecular particles, and the association factor is  $x$ . The following are some values of  $x$  determined in this way (which do not in every case agree with the values found by Ramsay's method): for glycol, 2; for glycerine, 1.75; for formic acid, 1.67; for acetic acid, 1.40; for methyl alcohol, 1.66; for ethyl alcohol, 1.51. Acetone, acetonitrile, and propionitrile are also associated. Hydrocarbons and ethers are as a rule very little associated. Of all substances, water has the highest association factor (higher than 8).

*Remark.*—In Traube's later publications he distinguishes:

(a) the material nucleus of the atom, and (b) the space in which this nucleus performs its oscillatory motions.

The constants on page 68 are composed of the sum of the volumes (a) and (b), but may continue to be called simply the atomic volumes.

The atomic volumes of several elements appear not to be very constant. Thus the value found for nitrogen varies between tolerably wide limits: from 1.5 (in certain primary amines) to 13 (in tri-isobutylamine). Similar variations have been detected for chlorine, bromine, &c., and this want of constancy is certainly a great drawback to the practical value of the system.

## OPTICAL PROPERTIES.—REFRACTION OF LIGHT

The velocity of transmission of light through any medium depends on the nature of the medium and more particularly on its density.

When a ray of light passes from one medium into another it is refracted in obedience to *Snell's law*. The incident ray, the refracted ray, and the normal to the boundary of the two media at the point of incidence, lie in one plane; and besides, there is a certain ratio between the sine of the angle of incidence and the sine of the angle of refraction, which is constant and characteristic for the two media.

The wave theory of light teaches us that this ratio of sines is the same as the ratio of the velocities with which the light wave traverses the two media respectively. This ratio is termed the *index of refraction*, and is usually denoted by  $n$ . If  $i$  is the angle of incidence,  $r$  the angle of refraction, and  $v$  and  $v_1$  the respective velocities of light in the two media, we have

$$n = \frac{\sin i}{\sin r} = \frac{v}{v_1}.$$

If we consider three media such as air, a liquid and glass, and if we determine the index for any two pairs, such as:

$$n \text{ (air/glass)} = N = \frac{v}{v_2}$$

$$\text{and } n \text{ (liquid/glass)} = n_1 = \frac{v_1}{v_2},$$

then we can find:

$$n \text{ (air/liquid)} = \frac{v}{v_1} = \frac{N v_2}{n_1 v_2} = \frac{N}{n_1}.$$

The limits of this book prevent us from going into a description of the various apparatus which may be used for the determination of the refractive index. A short account

of the theory of a typical apparatus may be given, and for this purpose we shall select *Pulfrich's Refractometer*.<sup>1</sup>

This apparatus is comparatively simple, and *Brühl's* improved form, furnished with a thermostat, is applicable over a long range of temperature.

Fig. 11 gives an idea of the arrangement.

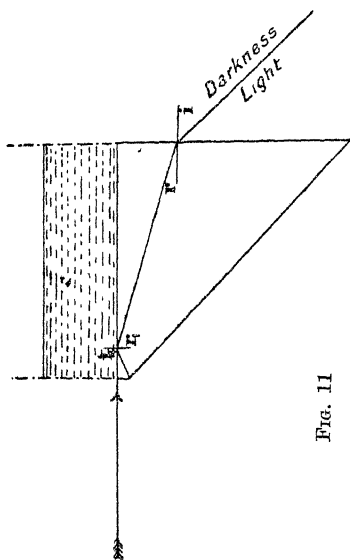


FIG. 11

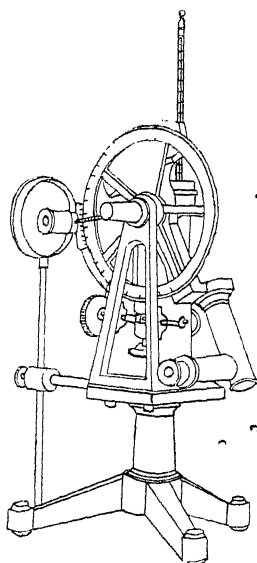


FIG. 12

The liquid or fused substance is placed in a small glass vessel which is fixed above a glass prism. The refractive index of this prism, which must be a right-angled one, must be known (it is generally 1.61).

A beam of light is allowed to enter the prism very close to and in the direction parallel to the horizontal surface of separation of the liquid and the glass (the angle of incidence,  $i_1$ , is then  $90^\circ$ ), and leaves the prism making

<sup>1</sup> Fig. 12 shows *Pulfrich's Refractometer*.

the angle  $i$  with the original direction. The angle  $i$  can be measured, and we are then in a position to calculate the value of  $n$ , i.e. the index of refraction for light passing from air into the liquid.

We know the index  $N$  for air/glass :

$$N (= 1.61) = \frac{\sin i}{\sin r}.$$

- For the light entering the glass from the liquid the angle of incidence is  $90^\circ$  ( $\sin i_1 = 1$ ), and we can calculate the index  $n_1$  liquid/glass in the following manner :

$$n_1 = \frac{\sin i_1}{\sin r_1} = \frac{1}{\sin r_1}.$$

- Now, by trigonometry,

$$\sin r_1 = \cos r = \sqrt{1 - \sin^2 r}$$

and, by transposing the first equation,  $\sin r = \frac{\sin i}{N}$ , therefore,

$$\sin r_1 = \sqrt{1 - \frac{\sin^2 i}{N^2}}, \text{ and consequently } = \frac{\sqrt{N^2 - \sin^2 i}}{N}$$

therefore 
$$n_1 = \frac{N}{\sqrt{N^2 - \sin^2 i}}.$$

If now we remember that  $n = \frac{N}{n_1}$ , then we find the index for air/liquid  $= n = \sqrt{N^2 - \sin^2 i}$ . There are tables which give the values of  $n$  directly for each value of  $i$ .

We thus obtain the index *air/liquid*, but if we wish to obtain the absolute index of refraction from vacuum into the liquid the value found must be multiplied by 1.00029. This correction, however, is generally omitted.

## REFRACTIVE POWER OF LIQUIDS

It is well known that different coloured rays of light are refracted to an unequal extent and that white light suffers dispersion. It is, therefore, necessary to study the index of refraction of a liquid by means of a monochromatic light, and for this purpose the yellow light of a sodium flame (D ray in the solar spectrum) is most often used, but sometimes also the red light of a hydrogen flame (C ray in the solar spectrum).

The *index of refraction* of a liquid varies with the temperature, the pressure, and in general with all the conditions which influence the density of the liquid or of the air. Attempts have been made to express the *refractive power* by a formula independent of these variations.

Newton for theoretical reasons gave the formula  $\frac{n^2 - 1}{d}$ .

The division by  $d$  is carried out in order that the refractive powers would be expressed as if all the liquids had the same density as water. Gladstone and Dale have shown that Newton's formula is inadmissible, and that the expression  $\frac{n - 1}{d}$  for the refractive power gives very much more constant values. The formula is better adapted than any other to express the refractive power of solutions and of mixtures. If we denote by  $n$ ,  $n_1$ , and  $n_2$ , and  $d$ ,  $d_1$ , and  $d_2$  the indices of refraction and the densities of a solution, the dissolved substance and the solvent respectively, then the equation

$$100 \frac{n - 1}{d} = p \frac{n_1 - 1}{d_1} + (100 - p) \frac{n_2 - 1}{d_2}$$

indicates the refractive power of a solution containing  $p$  parts of dissolved substance and consequently  $(100 - p)$  parts of solvent. And as  $n$ ,  $d$ ,  $n_2$ ,  $d_2$ , may be experimentally determined, we are in a position to calculate

$\frac{n_1 - 1}{d_1}$ , i.e. the refractive power of the dissolved substance (*Landolt and Willner, Schütt*).

More recently *L. Lorenz* and *H. Lorentz* have proposed the formula  $\frac{n^2 - 1}{(n^2 + 2)d}$ , which is now almost universally accepted. It gives very constant values for the same liquid under different conditions, and seems even applicable to vapours, as shown by experiments on ether, alcohol, chloroform, and water.

**MOLECULAR REFRACTION.**—By multiplying the refractive power of a substance by its molecular weight we obtain the molecular refraction. Using *Lorenz and Lorentz's* formula we have for the molecular refraction

$$\frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d}.$$

*The molecular refraction of a compound is composed additively of the refractive powers of the atoms contained in the molecule.*

• This rule being assumed, it is not difficult to ascertain, by empiric deductions, the atomic refractive powers of the principal elements contained in organic substances. *Brühl* has solved the problem in the following manner ( $n^2$  formula and for the red hydrogen ray).

First of all he found that in all the homologous series of fatty compounds a difference of  $\text{CH}_2$  in the composition corresponds to a difference of 4.57 in the molecular refraction. So that his first datum is:  $\text{CH}_2 = 4.57$ .

• From the molecular refraction of an aldehyde or of a ketone ( $\text{C}_n\text{H}_{2n}\text{O}$ ) he subtracts  $n$  times the value of  $\text{CH}_2$ , and thus finds the constant 2.328 for intra-radical oxygen ( $\text{O}''$ ).

By subtracting the molecular refraction of the hydrocarbon  $\text{C}_n\text{H}_{2n+2}$  from that of the corresponding alcohol  $\text{C}_n\text{H}_{2n+2}\text{O}$ , he obtains for extra-radical oxygen ( $\text{O}'$ ) 1.506; and the same constant can be deduced from the molecular



refractions of an acid and its corresponding aldehyde. By deducting six times the value of  $\text{CH}_2$  from the molecular refraction found for hexane ( $\text{C}_6\text{H}_{14}$ ) the constant (or rather double of it) is obtained for hydrogen:  $\text{H}_2 = 2.205$ . This same value is arrived at by deducting 1.506 for oxygen, and 9.14 for  $2\text{CH}_2$ , from the molecular refraction of alcohol ( $\text{C}_2\text{H}_6\text{O}$ ).

We have therefore :

$$\text{CH}_2 = 4.570$$

$$\text{H}_2 = 2.205, \text{H} = 1.103$$

$$\text{from which C} = 2.365.$$

It is only necessary to examine some substances containing chlorine, bromine, &c., in order to find the values given in the following table of atomic refractions :

—	For yellow light (sodium)	For red light (hydrogen) (Brühl)	Remarks
C	2.494	2.365	
H	1.051	1.103	
O'	1.517	1.506	Hydroxyl oxygen.
O''	2.281	2.328	Intra-radical oxygen.
O	1.679	1.655	Simple ether oxygen.
Cl	5.976	6.014	
Br	8.900	8.863	
I	14.120	13.808	
=	1.707	1.836	Double linkage between two carbon atoms.
≡		2.220	Triple linkage between two carbon atoms.

The refractive power of nitrogen is very variable. Its value in the different series increases in the following order : fatty amines—primary, secondary, tertiary, primary aromatic amines, hydrocyanic acid and nitriles, oximes, tertiary aromatic amines. The limits are 2.311 to 4.105 (for red hydrogen light) and 2.446 to 4.363 (for yellow sodium light).<sup>1</sup>

<sup>1</sup> See Brühl's publications in the *Berichte der deut. chem. Gesell.*, particularly Vol. 21, 1227 (1909).

The atomic constants deduced from the study of a certain number of compounds are useful for calculating the molecular refraction of other substances. In general, the theoretical number thus obtained agrees with that found by experiment. More than any others, *Landolt* and *Brühl* have contributed to our knowledge in this direction.

The determination of the molecular refraction of a substance is extremely useful for ascertaining or confirming the chemical constitution. Thus the molecular refraction of benzene indicates the presence of three double linkages in agreement with *Kekulé's* formula. Geraniol has the formula  $C_{10}H_{18}O$  and the characteristic properties of a primary alcohol. Its refractive index has been found to be 1.4745 for yellow light, from which we calculate the molecular refraction 48.71. The sum of the atomic refractions according to the preceding table is :

Carbon	. . . . .	$2.494 \times 10 = 24.940$
Hydrogen	. . . . .	$1.051 \times 18 = 18.918$
Oxygen (hydroxylic)	. . . . .	$1.517 = 1.517$
		<hr/> 45.375

The difference between this and the experimental result is  $48.71 - 45.375 = 3.335$ , which is very nearly twice the value for a double linkage ( $1.707 \times 2 = 3.414$ ). Geraniol thus appears to contain two double linkages; now, an alcohol  $C_{10}H_{18}O$  containing two double linkages cannot contain a ring and must therefore belong to the fatty series—a conclusion supported by the chemical character of the substance.

#### *Remarks*

1. The meaning of the factor  $(n - 1)$  in *Gladstone and Dale's* formula is easily understood. If we recall that

$$n = \frac{\sin i}{\sin r} = \frac{v}{v_1},$$

where  $v$  and  $v_1$  denote the velocity of transmission of the

light wave in the air and in the liquid, then it follows that

$$n - 1 = \frac{v - v_1}{v_1},$$

that is, it expresses the ratio of the excess of velocity in air over velocity in the liquid to the velocity in the liquid.

2. If we accept the theory of dielectrics of *Clausius* and *Mosotti*, and the electromagnetic light theory (*Maxwell*), we find that the factor  $\frac{n^2 - 1}{n^2 + 2}$  expresses *what fraction of the unit of volume of the substance is really occupied by the material*. The molecular refractive power

$$\frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d}$$

would therefore only be a corrected molecular volume—the material volume occupied by the atomic nuclei of the molecule (*Exner*, *Berichte der deut. chem. Gesell.* 18. R. 355; *Brühl*, *ibid.* 19. 2755).

3. There is an *approximately* constant ratio between this corrected molecular volume and the sum of the atomic volumes calculated by *Traube's* method (*Berichte*, 29. 2732).

$$\frac{\Sigma \text{ atomic volumes}}{\frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d}} = \text{about } 3.45.$$

This would, therefore, be the ratio between the oscillatory volume of the atoms and their real (nuclear) volume.

The presence of double linkages causes a diminution in this ratio. In order to observe any regularity it is necessary to use the maximum values found by *Traube* for the atomic volumes—thus for oxygen 5.5 must be taken.

4. For the molecular and atomic *dispersion of light*, reference should be made to *J. W. Brühl's* publications in the '*Berichte der deutschen chemischen Gesellschaft*' and in the '*Zeitschrift für physikalische Chemie*' (since 1887).

*Power of Rotating Polarised Light*

The determination of the rotatory power of a substance is made by means of an instrument whose function is based on the properties of polarised light.<sup>1</sup> The simplest apparatus consists of two nicol prisms (polariser and analyser) placed one behind the other, so that their axes lie in a straight line.

Suppose that the nicols are crossed, and that we send a pencil of *parallel light rays* along the axis of the polariscope. It is well known that the light, already weakened by the polariser, will be completely extinguished by the analyser, and that the field of vision will be quite dark.

If now we interpose between the crossed nicols a mono-refractive solid, for example a plate of glass or of a substance which crystallises in the regular system,<sup>2</sup> the extinction of the rays remains as before.

The darkness is not even diminished by the interposition of a crystalline substance belonging to the hexagonal or to the quadratic system, so long as we make use of a section cut perpendicularly to the optical axis and so placed between the nicols that this axis is parallel with the direction of the rays transmitted by the polariser.<sup>3</sup>

If, however, the experiment had been made with a *quartz* plate (and if, to avoid rotatory dispersion, monochromatic light had been used), the following would have been observed. In spite of the nicols being crossed, the field of vision would be more or less clear according to the thickness of the quartz plate; and in order to re-establish the original darkness the analyser would have to be turned

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<sup>1</sup> In order to understand the theory of the polarimeter a previous knowledge of optics is necessary, and particularly the phenomena of reflection, refraction, interference, and polarisation.

<sup>2</sup> The faces of the plate must, of course, be parallel.

<sup>3</sup> In the direction parallel with their optical axis the crystals in question (Iceland spar, &c.) behave as mono-refractive substances. It must be kept in mind that the rays from the polariser are supposed *parallel*. With convergent rays we observe the well-known coloured ring phenomenon.

through a certain angle to the right or to the left, depending on the variety (tetartohedral) of the quartz used. The quartz, therefore, had rotated the plane of vibration of the polarised rays coming from the first nicol.

Other crystalline substances, such as sodium chlorate, cinnabar, &c., possess an analogous rotatory power to that of quartz. This power is also possessed by a great number of substances which may be studied in the liquid state or in solution, and these frequently belong to the category of natural products;—vegetable acids, carbohydrates, glucosides, terpenes and camphors, alkaloids, albuminoids.

For the investigation of the *optical activity* of such substances or their solutions, they might be enclosed in a tube with transparent ends and interposed between two

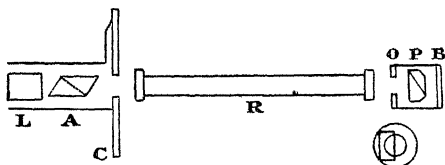


FIG. 13

crossed nicols, and the angle measured through which it was necessary to rotate the analyser to re-establish the original darkness of the field. But it is difficult to judge maximum darkness, and such a simple apparatus would not give sufficiently accurate results.

A number of improved *polarimeters* have been devised, which differ from each other chiefly in the means adopted to render the observation easy and accurate. As a typical apparatus we shall here describe *Laurent's half-shadow polarimeter*.

This instrument, intended for use with monochromatic yellow light (sodium flame), consists essentially of the following parts (Fig. 13).

A thin plate of potassium bichromate *B* for filtering the light, and thus only allowing the yellow to pass through.

A nicol polariser P.

A plate of quartz or mica cut *parallel* to the optical axis, and of such a thickness as to produce a difference of half a wave-length between the two rays which it gives by double refraction. This plate covers half of the opening o, as shown in the end view immediately below.

A tube R, closed at its ends by glass plates, to hold the liquid to be examined.

A nicol analyser A.

A small telescope L, focussed on the opening o.

A graduated circle c, and an index-pointer fastened to the analyser and rotating over c.

• Suppose the plane of vibration<sup>1</sup> of the nicol P be indicated in fig. 14 by the straight line OB, forming the

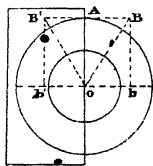


FIG. 14

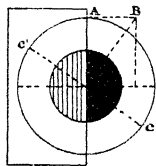


FIG. 15

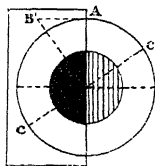


FIG. 16

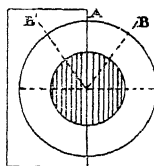


FIG. 17

angle  $\alpha$  with the principal axis OA of the quartz plate; then for the half of the field of vision to the right, the luminary vibration OB may be considered as the resultant of the two components OA and ob. For the half-field to the left (covered by the quartz plate) we have the components OA and ob', the latter being opposed to its corresponding component ob on account of the retardation of half a wave-length produced by the quartz. The components OA and ob' give the resultant OB'. If now we place the analyser in such a position that its plane of vibration is perpendicular to the direction OB (as indicated by cc' in fig. 15), the half of the field to the right will be

<sup>1</sup> This plane is parallel to the short diagonals of the end-face of the nicol prism.

dark, whilst the half to the left still allows light to pass through. If, on the contrary, the analyser be so rotated that its plane of vibration is perpendicular to  $OB'$  (as indicated by  $cc'$  in fig. 16), then the left half of the field is dark and the half to the right illuminated.

To obtain equality of illumination over the whole field, it is necessary to have the plane of vibration of the analyser perpendicular to  $OA$  (fig. 17). In this position the index-pointer on the analyser must be at the zero mark on the graduated circle  $c$  (fig. 18). If now a tube containing an optically active liquid be interposed, the vibrations  $OB$  and  $OB'$  will be both rotated through the same angle and in the same direction, and the equality of the illumination of the field will be disturbed. This equality is restored by rotating the analyser through an angle equal to that through which the vibrations  $OB$  and  $OB'$  have been rotated by the active liquid. This angle as indicated by the pointer is read off on the graduated circle.

The *angle of rotation* is proportional to the thickness of the layer of active liquid through which the light passes.

The value  $\frac{\alpha}{l}$ , where  $\alpha$  is the measured angle of rotation, and  $l$  the length in decimetres of the column of liquid, is constant for a substance, provided that we always work at the same temperature and with the same light.

In order to compare the effects produced by different active substances, the deviation per unit length (one decimetre)  $\frac{\alpha}{l}$  is divided by the density. The expression

thus obtained  $\frac{\alpha}{ld}$  is termed the *specific rotation*, and is usually represented by  $[\alpha]_D$  or  $[\alpha]$  according as the determination is carried out with yellow sodium light or with white light (in some saccharimeters daylight is used and equality of tint, instead of equality of illumination, is established).

For solid substances dissolved in an inactive solvent, the *specific rotation* is  $\frac{100 \alpha}{p l d}$ , where  $d$  is the density of the solution, and  $p$  the percentage of dissolved substance.

No matter how the rotatory power is determined, it is always more or less influenced by the temperature.

And furthermore, when we are concerned with the rotation of a solution, we find that it varies according to the nature of the solvent, the concentration<sup>1</sup> and the time which has elapsed between the dissolving and the polarimetric determination.<sup>2</sup>

Data concerning  $[\alpha]$  of a solution must always be accompanied by details of the temperature, concentration, &c.

The expression for the *molecular rotation* is

$$\frac{M [\alpha]}{100}$$

where  $[\alpha]$  is the specific rotation and  $M$  the molecular weight of the substance. The division by 100 is merely to reduce the size of the values.

• [NOTE BY TRANSLATOR.—We have learned two constants of rotation which can be used for comparing the effects of different substances. *Guye* has introduced a third which he terms the *molecular deviation*, and which he represents by  $[\delta]$ . This is calculated from the formula

$$[\delta] = \frac{\alpha}{l} \cdot \sqrt[3]{\frac{M}{d}}.$$

<sup>1</sup> By taking polarimetric observations of solutions of different concentrations of the same substance we can obtain a formula or a graphic curve expressing the variations of the rotation in terms of the concentration; and from this it is easy to calculate or extrapolate what the *true rotatory power* would be for a solution of maximum concentration, *i.e.* for the substance taken in the pure state.

<sup>2</sup> *Bj-rotation* (extra great activity) of dextrose and lactose freshly dissolved; *hemi-rotation* (reduced activity) of  $\gamma$ -lactose freshly dissolved. In order to obtain normal and constant rotations, the solution must either be allowed to stand for 24 hours, or be boiled for some time.



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No matter how the rotatory power is determined, it is always more or less influenced by the temperature.

And furthermore, when we are concerned with the rotation of a solution, we find that it varies according to the nature of the solvent, the concentration<sup>1</sup> and the time which has elapsed between the dissolving and the polarimetric determination.<sup>2</sup>

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$$[\delta] = \frac{\alpha}{l} \cdot \sqrt[3]{\frac{M}{d}}$$

<sup>1</sup> By taking polarimetric observations of solutions of different concentrations of the same substance we can obtain a formula or a graphic curve expressing the variations of the rotation in terms of the concentration; and from this it is easy to calculate or extrapolate what the *true rotatory power* would be for a solution of maximum concentration, *i.e.* for the substance taken in the pure state.

<sup>2</sup> *B $\gamma$ -rotation* (extra great activity) of dextrose and lactose freshly dissolved; *hemi-rotation* (reduced activity) of  $\gamma$ -lactose freshly dissolved. In order to obtain normal and constant rotations, the solution must either be allowed to stand for 24 hours, or be boiled for some time.

It is, therefore, the same as the rotation for unit length multiplied by the cube root of the molecular volume. The molecular rotation evidently reduces the rotation to that of columns of liquid proportional to the volumes of the different molecules; but, since the rotation is dependent on the thickness of substance through which the light passes, the rotation ought to be reduced to lengths corresponding to the diameters of the molecules, which is obviously accomplished by using the cube root of the molecular volume as in the formula for molecular deviation.]

CAUSE OF ROTATION.—*Reusch* has shown (1869) that it is possible to artificially construct a system which possesses optical activity, by superposing thin sheets of biaxial mica in such a way that the optical axes of the different sheets are arranged spirally. A similar spiral arrangement of the crystalline particles may be supposed to exist in quartz and in other optically active crystals. But it would be difficult to make the same supposition for liquids or solutions. In them the spiral structure must be the property of each molecule itself. This view is confirmed by an experiment of *Biot*, who showed that the vapour of an optically active liquid is itself optically active.

#### LE BEL AND VAN'T HOFF'S HYPOTHESIS

##### *Stereo-Chemistry of Carbon*

An asymmetric carbon atom is one which is united by its four valencies to four different elements or radicals. The chemical examination of optically active organic substances has shown that every one of them contains at least one *asymmetric* carbon atom. We may therefore find the cause of optical activity in the properties of the asymmetric carbon atom.

If we admit that the four valencies of a carbon atom are directed from the centre towards the four corners of a tetrahedron, it is easy to perceive that a substance of the

formula  $Cabcd$  corresponds to two non-superposable figures (in space) one of which is the mirror-image of the other.

In fig. 18,  $d$  is supposed above the plane of the paper at the summit of a pyramid. If we wish to trace a path round the base of this pyramid in the direction  $a-b-c$ , we must follow the same direction as the hands of a watch for the figure to the left, and the opposite direction for the figure to the right. Each of these figures is the mirror image of the other, and this enantiomorphism is found also in the optical and crystallographic properties of substances of the type  $Cabcd$ .

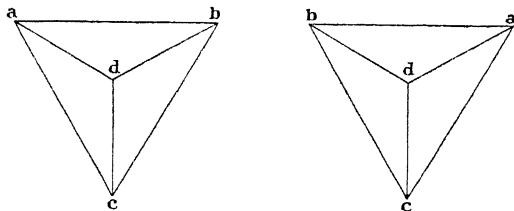


FIG. 18

For the sake of simplicity, we have taken the tetrahedron as regular, but, as the four valencies are saturated by elements or radicals of different *weight and volume*, it is probable that their centres of gravity are not equidistant from the central carbon atom, and that the molecule should be represented by an irregular pyramid.

The simplification of the figures, however, does not in any way affect our interpretation of the optical activity.

Let us assume (as in fig. 19) the active carbon atom at the centre of a regular tetrahedron with four monovalent elements or radicals at the four corners; and let us further suppose that the importance (weight and volume) of these elements or radicals decreases in the order 4, 3, 2, 1. We can then construct two non-superposable modifications.

Consider first the plane 1—2—4 of fig. 19, *a*.

The group 4, being more voluminous than group 2, is probably situated further away, with respect to the centre of gravity, from the central carbon atom (although its 'point of attachment' may be closer). In the same way

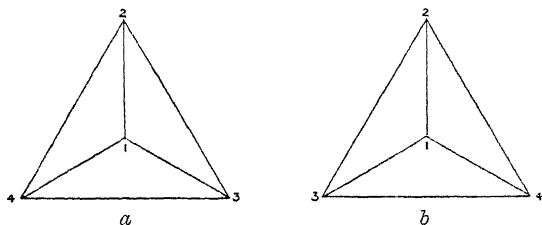


FIG. 19

group 2 is further away than group 1. From this it follows that the surface of 1—2—4 is a right-handed helical surface (one which we descend in passing in the direction in which the hands of a watch move). In order to make this clear, suppose a triangle representing the

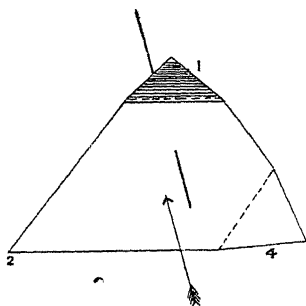


FIG. 20

surface 1—2—4 cut out of paper, and having a glass rod passed through its centre (fig. 20). Imagine the centre of gravity of the central carbon atom as situated on the glass rod behind the paper. The corner 4 should then be bent towards the front, *i.e.* removed further from the carbon atom. Similarly corner 1 is to be bent towards the back, *i.e.*

made to approach the carbon atom. Corner 2, unfolded, will then occupy an intermediate position.

A ray of light passing in the direction indicated by the arrow will meet a right-handed screw-surface, and the same happens to a ray coming in the opposite direction.

The surface 1—2—4 thus presents a right-handed screw to any ray of light, from whatever direction it may arrive.<sup>1</sup>

Let us now consider the behaviour of the *four faces* of the two enantiomorphic tetrahedra (figs. 19, *a*, and 19, *b*).

<i>a</i>				<i>b</i>			
Face	3—2—1	turns to the left		Face	3—2—1	turns to the right	
"	4—2—1	" "	right	"	4—2—1	" "	left
"	4—3—1	" "	left	"	4—3—1	" "	right
"	4—3—2	" "	right	"	4—3—2	" "	left

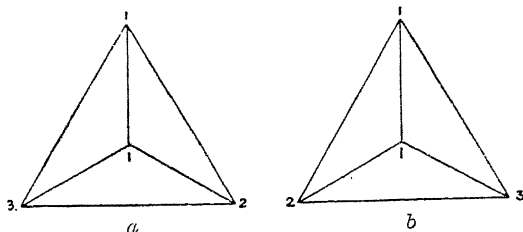


FIG. 21

• In both figures there are two faces of right rotation and two of left rotation. But the faces which turn to the right in one turn to the left in the other. It is very improbable that in a solution the molecules are all directed in a certain sense, and, consequently, the observed rotation

<sup>1</sup> The explanation of the phenomena of circular polarisation is due to *Fresnel*. This scientist has shown that in an optically active substance these phenomena are caused by the fact that the speed of transmission of a *circular polarised wave* varies according to the direction of its gyrotory motion. Thus, if a linear polarised ray enters an active substance under normal incidence, *i.e.* perpendicularly, it is split up into two circular polarised rays *r* and *r'*, a right one and a left one, and each of these is propagated at its own speed. On passing out from the substance these two rays, having the same speed in air, recombine to a linear polarised ray, whose plane of vibration makes an angle with that of the incident ray.

This explanation applies not only to quartz but also to substances containing an asymmetric carbon atom. For these the helical structure of the molecules appears to us to be the probable cause of the unequal speeds of transmission of the waves *r* and *r'*.

can only be the algebraic sum of the optical effects of the different faces of the dissolved molecules.

It is easy to show, by the theory we are now considering, that the presence of an asymmetric carbon atom is the necessary condition (*sine qua non*) of optical activity. In a substance of the type  $C_{1,1,2,3}$ , optical activity is not possible.

In fig. 21, *a*

The face 2—1—1	.	.	.	is inactive	
" " 3—1—1	.	.	.	is inactive	
" " 3—2—1	.	.	.	turns to the left	} equal and opposite effects
" " 3—2—1 (plane of the paper)	.	.	.	turns to the right	

In fig. 21, *b*

The face 2—1—1	.	.	.	.	is inactive
" " 3—1—1	.	.	.	.	is inactive
" " 3—2—1	.	.	.	.	turns to the right
" " 3—2—1 (plane of the paper)	.	.	.	.	turns to the left

These two last effects, in each case, being equal and opposite, the resultant is zero.

Let us now examine a molecule containing *two asymmetric carbon atoms*, and let us first take one of the type  $C_{1,2,3}-C_{1,2,3}$ , such as we have in tartaric acid. *Four modifications* are possible: the two asymmetric systems which together make up the molecule may be

- (1) both dextro-rotatory;
- (2) both lævo-rotatory;
- (3) one dextro- and the other lævo-rotatory—the resultant effect being zero;

or (4) a solution of two molecules of opposite activity is inactive, and from it an inactive substance crystallises out. But this substance can be *decomposed* into two active modifications; it is termed the *racemic form*.

The complete representation of the type  $C_{1,2,3}-C_{1,2,3}$  permits of an investigation of the effects of all the tetrahedral faces (figs. 22, 1, 2, 3, and 4).

Each half of the molecule being heavier and more

voluminous than any of the atoms or radicals 1, 2, 3, w shall represent it by 4.

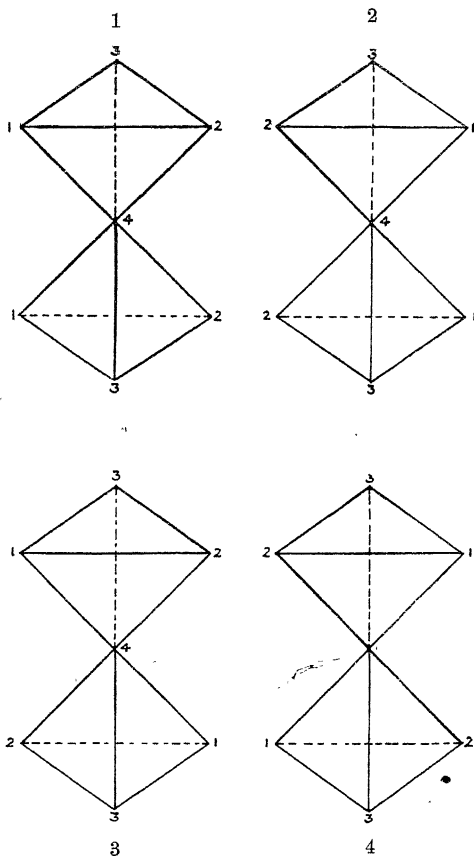


FIG 22

For the eight faces in fig. 22, 1, we find the following optical effects :



<i>In the upper tetrahedron</i>					<i>In the lower tetrahedron</i>				
Face	4—2—1	turns to the left			Face	4—2—1	turns to the left		
„	4—3—1	„ „ right			„	4—3—1	„ „ right		
„	4—3—2	„ „ left			„	4—3—2	„ „ left		
„	3—2—1	„ „ right			„	3—2—1	„ „ right		

In both tetrahedra the effect is again the difference between two dextro- and two lævo-rotations. The effect in each of the tetrahedra is the same and of the same sign; therefore, the whole is optically active.

A similar examination of fig. 22, 2, shows that it represents a substance equal in optical activity to the foregoing, but of opposite sign. Figs. 22, 3 and 4 represent the inactive modification which cannot be separated into two active forms. The two halves of the molecule have an equal optical effect, but of opposite sign. In fig. 20, 3, for example, we find:

<i>Upper tetrahedron</i>					<i>Lower tetrahedron</i>				
Face	3—2—1	is dextro-rotatory			Face	3—2—1	is lævo-rotatory		
„	4—2—1	„ lævo- „			„	4—2—1	„ dextro- „		
„	4—3—1	„ dextro- „			„	4—3—1	„ lævo- „		
„	4—3—2	„ lævo- „			„	4—3—2	„ dextro- „		

It is not necessary to give the theory for the type  $C_{1,2,3}-C_{4,5,6}$  in the same detail. Besides, this case comes under the *general rule* that a molecule which contains *n* asymmetric carbon atoms is capable of existing in  $2^n$  active modifications.

The following table demonstrates this rule. *a, b, c, &c.* represent different atoms or radicals united to the asymmetric carbon atom C. An arrangement of the letters like  $Cab^c d$  indicates a dextro-rotatory system, whilst a lævo-rotatory system is denoted by the arrangement  $Cab_c d$ . The table does not take account of the racemic forms.

*One Asymmetric Carbon Atom*

$\left. \begin{array}{l} Cab^c d \\ Cab_c d \end{array} \right\}$  Two ( $2^1$ ) active modifications are possible.

*Two Asymmetric Carbon Atoms*

$\left. \begin{array}{l} Ca^b c - Cd^e f \\ Ca^b c - Cd_e f \\ Ca_b c - Cd^e f \\ Ca_b c - Cd_e f \end{array} \right\} \begin{array}{l} \text{Four } (2^2) \text{ active modifications are possible.} \\ \text{For the simpler type } Cabc - Cabc \text{ the} \\ \text{forms 2 and 3 are identical and inactive.} \end{array}$

*Three Asymmetric Carbon Atoms*

$\left. \begin{array}{l} Ca^b c - Cd^e - Cf^g h \\ Ca^b c - Cd_e - Cf_g h \\ Ca^b c - Cd_e - Cf^g h \\ Ca^b c - Cd_e - Cf_g h \\ Ca_b c - Cd^e - Cf^g h \\ Ca_b c - Cd^e - Cf_g h \\ Ca_b c - Cd_e - Cf^g h \\ Ca_b c - Cd_e - Cf_g h \end{array} \right\} \begin{array}{l} \text{Eight } (2^3) \text{ active modifications} \\ \text{are possible.} \end{array}$

A few examples may now be quoted in support of the theory the outlines of which have just been given.

*Substances with One Asymmetric Carbon Atom.*—We foresee two active modifications and one inactive (by mixture of the active ones).

*Ethylidene-lactic acid :*

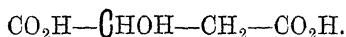


We know :

1. the *inactive* acid : ordinary-lactic acid.
2. the *dextro-rotatory* acid. This exists in the substance of the muscles. It can be artificially prepared by cultivating *Penicillium glaucum* in fermentation ammonium lactate; the *laevo-rotatory* modification is destroyed in greater quantity, causing the residue to become *dextro-rotatory*.

3. The *laevo-rotatory* acid. This is produced by the action of a certain bacillus, found in some Hungarian wells, on cane sugar. It can also be obtained by crystallisation of the strychnine salt of the inactive acid, when the salt of the *laevo-rotatory* form separates out first.

*Malic acid :*



The following modifications are known :

1. The *levo-rotatory* acid—obtained from the berries of the mountain ash.

2. The *racemic* acid (inactive by mixture)—obtained artificially :

(a) by reduction of racemic tartaric acid by hydriodic acid.

(b) by the action of water on fumaric acid (boiling the fumaric acid with a dilute solution of caustic soda).

3. The *dextro-rotatory* acid—obtained :

(a) by reduction of dextro-tartaric acid by hydriodic acid.

(b) by resolving the racemic form. A saturated solution of inactive cinchonine malate is induced to crystallise by sowing with a crystal of the *levo-* malate of the same base. In this way *Bremer* has, surprising as it may appear, induced a crystallisation of the *dextro-* malate ('Berichte,' 13. 351. (1880)).

acetaldehyde gives  $\alpha$ -allylpyridine, which, reduced with metallic sodium, gives inactive coniine.

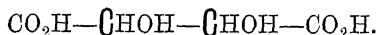
3. If to a saturated solution of inactive-coniine acid tartrate a crystal of dextro-coniine acid tartrate be added, the dextro- salt crystallises out, leaving the salt of *lævo-coniine* in the mother liquor.

Many other examples might be cited, such as valerianic acid, amyl alcohol, asparagine, &c.

*Substances with Two Asymmetric Carbon Atoms.*—

Four modifications are possible, namely, a dextro- and a lævo-, an inactive (which cannot be resolved), and a racemic form.

*Tartaric Acid:*



Our knowledge of the optical isomers of this acid is chiefly due to *Pasteur's* researches.

We know the following four varieties:

1. The *dextro-rotatory* acid. This is the ordinary tartaric acid obtained from cream of tartar. It separates without water of crystallisation in monoclinic prisms. It is dextro-rotatory in aqueous solution. Its salts frequently have small hemihedral faces on their crystals.

2. The *racemic* acid which crystallises with one molecule of water. It can be obtained by dissolving an equimolecular mixture of the dextro- and lævo- acids. To prepare the racemic acid the dextro-acid is heated with about a tenth of its weight of water to  $175^\circ\text{C}$ . Inactive and racemic acids are both formed, and can be separated by crystallisation.

The racemic acid crystallises with one molecule of water in efflorescent rhombic crystals. It is less soluble than the dextro-acid and forms salts similar to those of the dextro-acid but without any hemihedral facets.

The racemic acid can be separated into the two active forms in the following manner. A solution of the acid sodium salt is saturated with ammonia and the solution is

allowed to crystallise by spontaneous evaporation: The crystals of the double sodium ammonium salt which separate out are of two sorts and are recognised by the hemihedral faces which they possess. The crystals are then mechanically separated, and it is found that one sort is dextro-rotatory and gives dextro-tartaric acid, whilst the other sort is lævo-rotatory and gives the lævo-acid.

In order that this decomposition of the double salt may take place, the crystallisation must go on at a temperature below  $28^{\circ}$ . At higher temperatures a double sodium ammonium racemate is formed.

*Penicillium glaucum* destroys by preference the dextro-acid; this offers us another means of decomposing racemic acid.

### 3. The lævo-rotatory acid.

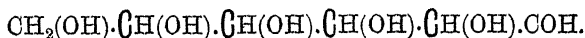
We have just seen how it is prepared. It is very similar to the dextro-acid, but rotates the plane of polarisation to the left. Its salts are similar to those of the dextro-acid, but are lævo-rotatory.

Dextro- and lævo-tartrates are frequently isomorphous, but show opposite hemihedral facets (mirror-images of each other).

### 4. The inactive acid.

To obtain this, the dextro-acid is heated with a tenth of its weight of water to  $165^{\circ}$  for two days. The mixture obtained consists of dextro-acid, racemic acid, and the inactive acid. The isolation of this last is based on the solubility of its acid potassium salt (the other acid tartrates are only sparingly soluble in water).

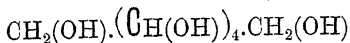
*Substances with four asymmetric carbon atoms.—For hexose*



sixteen ( $2^4$ ) active modifications are possible as well as eight inactive racemic forms.

In the case of the *hexites* the similarity of the end-

groups reduces the number of possible isomers. Still, for the formula



we can expect ten optical isomers, two of which are inactive by intramolecular compensation, and four racemic modifications.

The structure of these substances has been elucidated by *E. Fischer* and his students.

*Remarks* : 1. Thanks to the work of *Guye, Frankland*, and a few other chemists, we are now beginning to learn the laws which regulate the rotatory power.

In the first place, it would seem that, so long as the order of the size of substituting groups attached to the asymmetric carbon atom of a substance remains unchanged, so long does the direction of the rotation remain the same.

This can be seen from tartaric acid ; the dextro-acid gives neutral esters (diethyl tartrate, for example) which are also dextro-rotatory. The diacetyl derivative of this acid, however, is lævo-rotatory ; but here the order of the size of the groups is modified, for the group  $\text{O.CO.CH}_3$  (originally  $\text{OH}$ ) is greater than the group  $\text{CO}_2\text{H}$ .

This rule, however, is not quite general, an exception to it being found in the etherification of lævo- amyl alcohol. In this case there can be no doubt that it is the heaviest group which is made heavier ( $\text{CH}_2\text{OH}$  becomes  $\text{CH}_2\text{OR}$ ), and therefore the order is not changed ; yet the rotation of the ether is in the opposite direction to that of the original alcohol. From this we see that, besides their relative size, the *specific influence* of the groups must be taken into account.

When we examine an homologous series derived from the same active nucleus, the regularities become more apparent if we consider the *molecular rotation*. For the esters of lævo-menthol *Tchugaeff* has found the following numbers :

	Specific rotation at 20° [ $\alpha$ ] <sub>D</sub> <sup>20°</sup>	Molecular rotation at 20° [M] <sub>D</sub> <sup>20°</sup>
Menthol . . . . .	— 50·0°	— 78°
Menthyl formate . . . . .	— 79·52	— 146·3
„ acetate . . . . .	— 79·42	— 157·3
„ propionate . . . . .	— 75·51	— 160·2
„ <i>n</i> -butyrate . . . . .	— 69·52	— 156·9
„ <i>n</i> -valerate . . . . .	— 65·55	— 157·3
„ caproate . . . . .	— 62·07	— 157·7
„ cenanthate . . . . .	— 58·85	— 157·7
„ caprylate . . . . .	— 55·25	— 155·8

Whilst the specific rotation exhibits scarcely any regular progression, the molecular rotation rapidly rises to a maximum, and then remains fairly constant. The esters of borneol, of active amyl alcohol, and of certain acids exhibit the same kind of regularity.

The influence of the phenyl (C<sub>6</sub>H<sub>5</sub>) group is very interesting. For menthyl benzoate, the three menthyl toluates, and the phenacetate and phenylpropionate of the same radical, the following molecular rotations have been found :

	[M] <sub>D</sub> <sup>20°</sup>
Menthol benzoate. . . . .	— 236·3°
„ ortho-toluate . . . . .	— 231·3°
„ meta-toluate . . . . .	— 241·0°
„ para-toluate . . . . .	— 252·5°
„ phenacetate . . . . .	— 190·7°
„ phenylpropionate . . . . .	— 161·9°

From a comparison of these numbers with those of the preceding table we may conclude that in the esters of menthyl the acid radicals only exert an influence on the molecular rotation by that part which is nearest the centre of asymmetry. Because (1) the action of the acetyl radical is just as powerful as that of its higher homologues, and (2) the great influence of phenyl only makes itself felt strongly in the benzoyl- and toluy-esters (*Tchugaeff*, 'Berichte der deut. chem. Gesell.' 1898, page 1778).

2. Substances which are active in solution are frequently inactive in the crystalline state, and *vice versa*. *Rammelsberg* ('Berichte d. d. ch. G.' 1869) distinguishes the following cases :

(a) Substances active only in the crystalline state: quartz, sodium chlorate, sodium bromate, and Schlippe's salt.

(b) Substances which are active in solution but inactive in the crystalline state: tartaric acid, malates, asparagine, the sugars, camphor, &c.

(c) A single substance active both in solution and in the crystalline form: strychnine sulphate (with water of crystallisation). (See note on page x.)

From these peculiarities *Rammelsberg* concluded that crystalline particles are not simple molecules, but are multimolecular associations. For substances of series *a*, a helical structure must be attributed either to the molecules in the crystalline particle or to the crystalline particles in the crystal. For substances of series *b* the dissolved isolated molecules must possess a rotatory power which they lose in forming the aggregates of the solid.

These conclusions have been partly confirmed. Thus, when the association factor of a solid substance is determined by *I. Traube's* method, it is generally found to be almost 2.<sup>1</sup> There remains, however, the question how the juxtaposition of two active and identical molecules can produce an inactive aggregate. Here no pretence is made of giving a final solution of this difficult problem, but a tentative interpretation by means of figures may not be out of place. The separate tetrahedra of fig. 23 represent two active and identical molecules (because they are asymmetric and superposable). After joining two homonymous edges (2—3), we get a double molecule, and the inactivity of this can be shown by applying the principles on which we based the theory of optical isomers.

<sup>1</sup> The tartaric acids are bimolecular in the crystalline state but monomolecular in solution. The liquid tartaric acid esters are monomolecular.



But we shall not further dwell on these considerations, especially as the problem would appear to be solved in quite another sense. *Hermann Traube* ('Jahrbuch für Mineralogie,' Beilageband, 1896) has found that patchouli camphor, as well as ordinary camphor, has the same rotation in the crystalline form and in solution.<sup>1</sup> This mineralogist believes that the same would be found to be the case for many other active substances, if crystals of

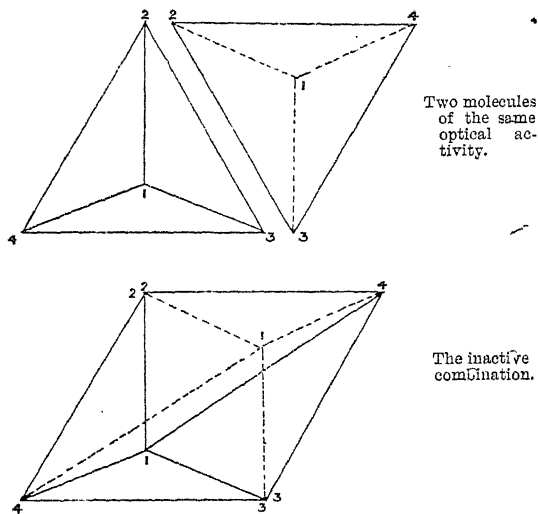


FIG. 23

them large and clear enough could be obtained to allow of polarimetric observations being made on a sufficiently thick section. If this could be confirmed, then *Rammelsberg's* classification could no longer hold; at least categories *b* and *c* would then form only one class, and the theoretical interpretation of the facts would be very much simplified. It would then suffice to distinguish between rotatory power due to asymmetry in the molecule and permanent through

<sup>1</sup> *J. Chem. Soc.* 70, ii. 509.

all states of aggregation, and crystalline rotatory power due to the arrangement of the molecules in the crystalline particle. In crystallised bodies possessed of both these causes of optical activity, the two effects, although absolutely independent of each other, would be found to combine.

3. *H. Landolt* has recently shown ('*Berichte d. d. ch. G.*' 1896) that finely pulverised sodium chlorate (in grains of diameter 0.004 to 0.012 millimetre) retains its rotatory power. This shows that the reduction to this state of division has not destroyed the crystalline structure.

4. Generally speaking, it may be asserted that, as yet, no organic substance endowed with rotatory power has been discovered which does not contain at least one asymmetric carbon atom. But substances are known which contain asymmetric carbon atoms and yet are optically inactive. This circumstance, however, is in no way in opposition to *Le Bel and van't Hoff's* theory, since the substances may belong to the inactive or racemic types. Most artificial substances, prepared either synthetically or by transformations of natural products at high temperatures, belong to the racemic type. The chief methods of resolving this type into the constituent dextro- and lævo- modifications are these :

*a. Crystallisation of a salt.*—Example: double tartrate of sodium and ammonium (must be crystallised below a certain temperature).

*b. Crystallisation of a salt formed with an optically active acid or base.*—Example: cinchonine malate in the preparation of dextro-malic acid.

*c. The action of certain fungi* (*Penicillium Glaucum*, *Aspergillus Niger*, yeast plants, &c.).—Example: the decomposition of racemic (tartaric) acid by *Penicillium*; the fungus feeds chiefly on the dextro-acid, and if the cultivation be stopped at the correct moment the lævo-acid can be isolated.

The same fungus living at the expense of the racemic form of amyl alcohol destroys the dextro- modification first.

In his researches on the carbohydrates, *E. Fischer* has on more than one occasion made use of this mode of resolving the racemic modifications.

## APPENDIX

In order to complete our study of the *stereo-chemistry* of carbon, it is necessary to say a word on a kind of isomerism peculiar to substances containing one or more *double linkages* in the molecule.

In the stereo-chemical interpretation of the behaviour of substances towards polarised light, which we have just discussed, it has been assumed that two carbon atoms united together by a single bond are at liberty to execute rotatory movements round their common axis.<sup>1</sup> If this were not the case, if there were a rigid union between the two carbon atoms, then we ought to find a very much greater number of isomers than really exist.

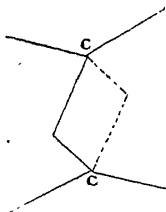


FIG. 24

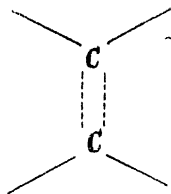


FIG. 25

But this free rotation is no longer possible when two neighbouring carbon atoms become united together by two bonds. And in this case we meet with isomers the interpretation of which requires further stereo-chemical considerations.

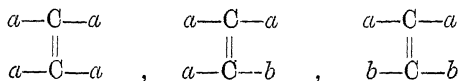
In Fig. 24 the two bonds by which the carbon atoms

<sup>1</sup> According to *Wislicenus*, the atoms or groups carried by the two carbon atoms exercise a directive action on each other, and the carbon atoms revolve until the system takes up the most stable configuration.

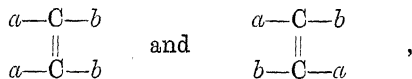
are held together are shown in perspective as situated in a plane perpendicular to that of the paper. In fig. 25 a simpler arrangement is adopted.

The possibility of isomerism depends on the similarity or variety of the atoms or groups which saturate the four free valencies.

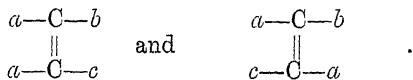
Of such types as :



there is only one form possible. Isomeric forms are, however, possible for the types,

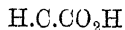


and for

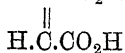


The two atoms or groups *a* may be both on the same side, or they may be on different sides of the plane in which the two carbon atoms and the two bonds joining them lie. In the first case we have the *cis* or malenoid form, and in the second case the *trans* or fumaroid form. Examples of this class of isomerism are very numerous.

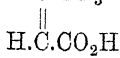
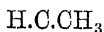
Fumaric acid,



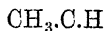
Maleic acid,



Crotonic and isocrotonic acids,



and



In his researches on the carbohydrates, *H. Fischer* has on more than one occasion made use of this mode of resolving the racemic modifications.

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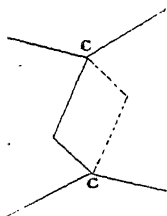


Fig. 24

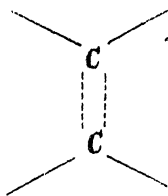


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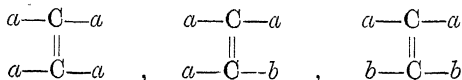
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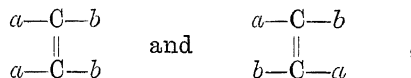
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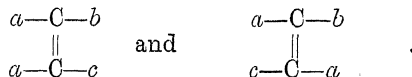
Of such types as:



there is only one form possible. Isomeric forms are, however, possible for the types,

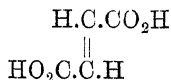


and for

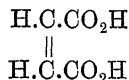


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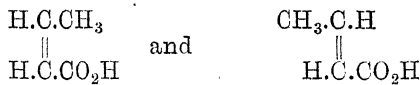
Fumaric acid,



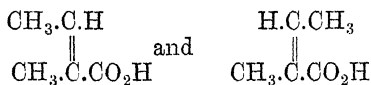
Maleic acid,



Crotonic and isocrotonic acids,

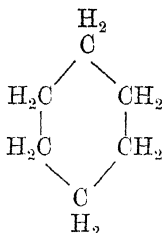


Angelie and tiglic acids,

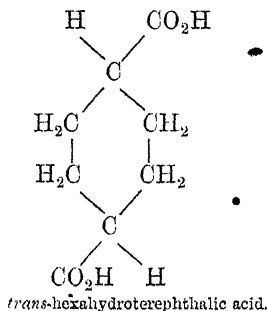
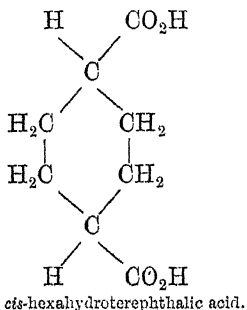


Similar examples are oleic and elaidic acids, erucic and brassic acids, &c.

We have now become acquainted with two causes of stereo-chemical isomerism: the asymmetry of the carbon atom, and double linkage between two carbon atoms. These two causes may produce very interesting combined effects in polymethylene ring compounds. Let us take as example the ring of six carbon atoms. *Hexamethylene* or benzene hexahydride has the formula  $\text{C}_6\text{H}_{12}$  and the constitution:

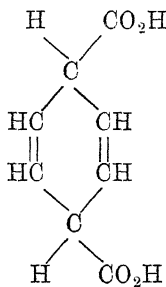
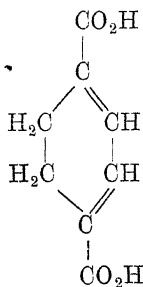
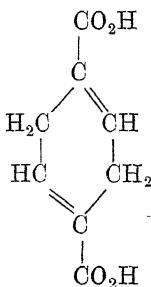
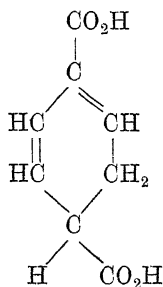


The replacement of two of the hydrogen atoms (attached to different carbon atoms) gives rise to the ordinary ortho-, meta-, para- isomerism and besides to stereo-chemical isomers. We know two hexahydroterephthalic acids, a *cis* and a *trans* modification:



For the corresponding *meta*- and *ortho*-derivatives the effect becomes more complicated owing to the asymmetry of the carbon atoms to which the  $\text{CO}_2\text{H}$  groups are linked.

The derivatives of dihydro- and tetrahydrobenzene are still more complicated. As an example, let us take *dihydroterephthalic acid*. The position of the double bonds determines four cases of isomerism :



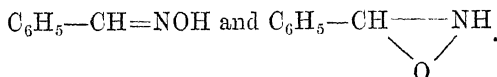
The first of these four formulæ contains an asymmetric carbon atom, and so we conclude that optically active isomers of it exist. The last formula is a *cis*-modification and so a corresponding *trans*-form must also exist.

In reality, *Baeyer* has isolated 5 dihydroterephthalic acids.

STEREO-CHEMISTRY OF NITROGEN.—Cases of isomerism are known for some substances containing nitrogen, and



attempts have been made to explain these by stereo-chemical considerations. Here we shall only mention the aldoximes and the ketoximes, hydroxamic acids and certain analogous compounds. We know, for example, two benzaldoximes to which *Beckmann* assigns the formulæ



*H. Goldschmidt* has studied the compounds of these substances with phenyl isocyanate and concludes that the  $\alpha$  and  $\beta$  modifications of benzaldoxime have the same structural formula. *Werner and Hantzsch* have proposed the following stereo-chemical formulæ :



This theory is, however, not quite definitely established, and *Beckmann*, amongst others, has furnished fresh experimental evidence in support of his view. According to the late *V. Meyer*, the cause of this isomerism is to be found in the constitution of hydroxylamine ('*Berichte*,' **23**. 2407).

But it is now time to leave the domain of pure chemistry and pass on to subjects more in harmony with the title of this book.

### MAGNETIC ROTATION

Some substances, which themselves are possessed of no optical activity, may acquire a rotatory power when placed under the influence of a powerful electro-magnet. This very interesting phenomenon was discovered by *Faraday* (in 1845), and its development from the chemical point of view is due almost entirely to *W. H. Perkin, sen.*

*Perkin's* method of examination is, to place a polarimeter tube containing the liquid or solution, axially

between the perforated magnet-poles (or perforated armatures). After exciting the magnet, we find that a rotatory power has been developed, to the right or to the left, according to the direction of the current, and to a greater or less extent, depending on the intensity of the magnetic field and the nature of the liquid.

Fig. 26 shows the arrangement.

In order to obtain comparable results it is necessary to employ always the same light (monochromatic sodium

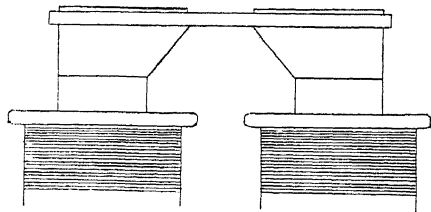


FIG. 26

light), and work at the same temperature ( $15^{\circ}\text{C.}$ ) in tubes of the same length (10 centimetres). The magnetic rotation of a substance is expressed by the formula

$$\frac{\alpha M}{d},$$

$\alpha$  being the observed angle,  $M$  and  $d$  the molecular weight and density of the substance under investigation.

Water is chosen as standard of comparison, and *Perkin* terms the quotient of  $\frac{\alpha M}{d}$  for any substance by the corre-

sponding value  $\frac{\alpha' M'}{d'}$  for water, the *molecular magnetic rotation* of the substance. In the determination of the angles  $\alpha$  and  $\alpha'$ , the same electric current must be used. That is, the magnetic molecular rotation is

$$\frac{\alpha M d'}{\alpha' M' d}$$

The molecular magnetic rotatory power is an additive property for organic substances. *In the same homologous series, its general expression is :*

$$a + nb.$$

The characteristic  $a$  is a special number for the series under consideration, whilst the constant  $b$  which corresponds to a difference of  $\text{CH}_2$ , is invariably equal to 1.023;  $n$  denotes the number of carbon atoms contained in the molecule.

In order that substances follow this rule, it is necessary that they are truly homologous. Isomeric substances, one with a normal carbon chain and the other with side chains, have not the same molecular magnetic rotation.

The following table gives the principal values found for the characteristic  $a$  :

Substances	—	$a$	—	$a$
Paraffins: $\text{C}_n\text{H}_{2n+2}$ . . .	normal	0.508	iso-	0.621
Alcohols: $\text{C}_n\text{H}_{2n+2}\text{O}$ . . .	"	0.699	secondary or iso-	0.844
Ethers, simple or mixed . . .	"	0.642	iso-	0.932
Aldehydes: $\text{C}_n\text{H}_{2n}\text{O}$ . . .	"	0.261	"	0.375
Ketones . . . . .	"	0.375		
Acids: $\text{C}_n\text{H}_{2n}\text{O}_2$ . . .	normal	0.393	iso-	0.509
Acetic esters starting with ethyl acetate . . .	"	0.370	"	0.485
Ethyl esters starting with ethyl propionate . . .	"	0.337	"	0.449
Ethyl esters of the succinic acid series . . .	"	0.196		
Chlorides: $\text{C}_n\text{H}_{2n+1}\text{Cl}$ . . .	"	1.988	secondary or iso-	2.068
Bromides: $\text{C}_n\text{H}_{2n+1}\text{Br}$ . . .	"	3.816	"	3.924
Iodides . . . . .	"	8.011	"	8.099
Ethyl esters of unsaturated acids: $\text{C}_n\text{H}_{2n-2}\text{O}_2$ . . .	"	1.451		

Abnormal values (too high) have been found for the molecular magnetic rotation of the first two or three members of homologous series, and generally, for substances of low molecular weight.

Just as we saw that the refractive power is very much influenced by the constitution of the molecule, so also is the magnetic rotation. A double linkage, for instance, very considerably increases the characteristic  $\alpha$ , as may be gathered from the last figure of the first column of numbers in the table. But this increase is very far from constant; the difference between the molecular magnetic rotations of vinyl- and ethyl-bromides is 0.869, whilst between their iodides it is 1.708.

The observations on magnetic rotation of carbon compounds have not led to anything like the same regularities as we have discovered for the refraction and atomic volumes.

It may be added that magnetic rotation observations have been carried out on inorganic substances; but the interpretation of the rotatory powers of acids, bases, and salts in aqueous solution appears to offer great difficulty.

We cannot enter further into this exceedingly interesting subject, the practical work on which demands resources which are not at the disposal of every chemist.

Those specially interested in the subject would do well to consult *Perkin's* publications in the 'Journal of the Chemical Society,' and also *Jahn* ('Wiedemann's Ann.' 43. 280), *Wachsmuth* (ibid. 44. 377), and *Schönrock* ('Zeitschrift f. phys. Chem.' 11. 753).

## SOLUTIONS

### *Molecular Volume of Dissolved Substances*

The density of a solution is determined in the same way as that of a homogeneous liquid, namely, by means of a pycnometer, or by *Westphal's* balance.

If we consider a quantity of a solution containing one gram-molecule of dissolved substance, it is evident that the volume occupied by the substance is equal to the volume

of the solution less the volume of the solvent. This is expressed by the equation :

$$v_m = \frac{M + ag}{d} - \frac{ag}{\delta} \text{ cubic centimetres.} \quad (1)$$

where  $v_m$  is the molecular volume of the substance,  $M$  its molecular weight,  $ag$  the weight of the solvent in grams,  $d$  the density of the solution, and  $\delta$  the density of the solvent ( $d$  and  $\delta$  being taken at  $15^\circ$  and with respect to water at its maximum density).

By means of this formula, it has been possible to show that the molecular volume in solution is an additive property. Indeed, the molecular volume of many salts remains unchanged by the substitution of one metal for another, as, for instance, sodium for lithium or hydrogen, or the molecular volume is altered by a constant amount, for instance, by the substitution of potassium for sodium.

But this formula very often leads to results which are too small or even negative.

From the following considerations, *I. Traube* has been able to correct the formula. If we determine the molecular volume of a *non-associated substance in the homogeneous or pure state* :

$$v_m = \frac{M}{d},$$

and the molecular volume of the *same substance in aqueous solution* :

$$v_m = \frac{M + ag}{d} - \frac{ag}{\delta},$$

we quite generally find

$$v_m = v_m - 13.5 \text{ c.c.} \quad (2)$$

It is probably not the volume of the dissolved substance which diminishes by 13.5 c.c., but by the formation of new attractions between heterogeneous molecules, the total volume, and more particularly the volume of the solvent

(water), is diminished by that amount. Be that as it may, the contraction produced affects the value of the molecular volume as calculated by equation (1).

We have already seen that the molecular volume of a homogeneous substance is equal to the sum of the atomic volumes increased by the co-volume 25.9 c.c. In aqueous solution the same rule holds good, but the co-volume is 13.5 units smaller, and so we have the following equations for the molecular volume of a substance in the pure state and in solution :

$$v_m = \frac{M}{d} = \Sigma \text{ atomic volumes} + 25.9 \text{ c.c.} \quad (3)$$

$$v_m = \frac{M + aq}{d} - \frac{aq}{\delta} = \Sigma \text{ atomic volumes} + (25.9 - 13.5) \text{ c.c.} \quad (4)$$

For dilute (1 to 3 per cent.) aqueous solutions at temperatures near 15°, we can calculate the sum of the atomic volumes from *Traube's* constants given on page 68. Every ring formation of six carbon atoms produces a further contraction of 8.1 c.c. Double or triple linkage between two carbon atoms seems to be without influence on the resulting volume (?).

This theory has been applied to a large number of organic liquid substances and even to some solids: acids, alcohols, ethers, ketones, amides, amines, phenols, &c., and the difference between the calculated and the experimental  $v_m$  has only rarely been as much as two or three units.

This is due to the fact that irregularities due to polymerised or associated particles do not present themselves. In aqueous solution the molecules seem to be as simple as in the gaseous condition. Even for substances which associate very readily, such as methyl alcohol, acetic acid, and glycerine, the molecular volumes in dilute solution are normal, corresponding to the values calculated by equation (4). Complications, however, arise with the influence of structural peculiarities which cannot yet be satisfactorily

dealt with: thus the *cis* and *trans* isomers or position-isomers of the aromatic series have not always the same molecular volume in solution.

*Remarks.*—1. Equation (4) is, of course, only applicable if the assumed molecular weight be equal to the real molecular weight. Thus the determination of the density of a solution may be used to control the molecular weight of the dissolved substance.

2. We have seen that generally

$$v_m = v_m - 13.5 \text{ c.c.}$$

This relation, however, is not so simple if the homogeneous liquid substance is made up of polymerised particles. In this case, if the polymerised particle consists of  $n$  molecules,

$$v_m = \Sigma \text{ atomic volumes} + \frac{25.9}{n}$$

$$v_m = \Sigma \text{ atomic volumes} + (25.9 - 13.5)$$

and, therefore,

$$v_m = v_m + 12.4 - \frac{25.9}{n}$$

3. For the *majority* of organic substances, liquid and solid, the molecular volume in concentrated solution in such solvents as benzene, chloroform, acetic acid, &c.,<sup>1</sup> has been found to be equal to the sum of the atomic volumes increased by a co-volume, 25.9 c.c. The dissolved substance is, therefore, present as simple molecules, and, there being but a very slight contraction, the co-volume retains its full value.

4. Solid substances, taken as such, on the contrary, give as molecular volume

$$\frac{M}{d} = \Sigma \text{ atomic volumes} + \frac{25.9}{n}$$

which proves that solids are generally not made up of simple molecules but of polymerised particles.

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<sup>1</sup> Ethyl and methyl alcohol are not to be included.

5. We shall see later that the molecules of acids, bases, and salts undergo dissociation when dissolved in water. A molecule of sodium chloride for instance, does not remain in solution as a single molecule, but gives rise to two particles ( $\text{NaCl} + \text{HOH} = \text{NaOH} + \text{HCl}$ ). If the solution is sufficiently dilute, then this dissociation becomes complete, and the number of dissolved particles is thus doubled and consequently the contraction of the solution is doubled (although no supplementary co-volume has to be added). We then have

$$v_m = \Sigma \text{ atomic volumes} + (25.9 - 2 \times 18.5).$$

In a later chapter on the constitution of salt solutions it will be explained how the *degree of dissociation* may be taken into account in these calculations.

## OSMOTIC METHODS

We have already learned some methods of determining the molecular weight of a substance, namely (1) by means of the vapour density if the substance is volatile, and (2) Traube's density method if the quantitative composition and constitution of the liquid or solid substance is accurately known.<sup>1</sup> And now we intend to devote a few pages to some comparatively simple methods of determining the molecular weight of *dissolved substances*.

### *Osmotic Pressure*

The osmotic pressure of a solution is measured with the help of an apparatus with *semipermeable walls*. To set up this apparatus, a semipermeable cell is constructed as follows: a small porous cell (such as is used for electric batteries) is carefully washed, then impregnated with a 3 per cent. solution of copper sulphate. It is then rinsed out with

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<sup>1</sup> Double linkages, ring-formations, manner in which the oxygen or nitrogen is combined, &c., must be taken into account.



distilled water, gently wiped with bibulous paper, then filled with a 3 per cent. solution of potassium ferrocyanide. At the same time the cell is immersed in a 3 per cent. solution of copper sulphate. Where the solutions meet inside the walls a deposit of copper ferrocyanide is formed. According to *Pfeffer* (from whom these details are taken), it is essential that the precipitate be deposited on the inner side of the cell wall and a little inside the wall. And further, the deposit should be thin, adherent, and absolutely continuous. It is not easy to satisfy all these conditions.

Other substances, besides copper ferrocyanide, may be used, and in fact, ferric hydrate, silicic acid, calcium phosphate, gelatine tannate, &c., have been used successfully.

The cell thus prepared will have become less permeable to water. Water can now pass through only slowly, and only when assisted by a certain pressure. But if, instead of water, we put a solution of an organic or inorganic substance into the cell, a still higher pressure is required to cause drops to filter through, and what passes through is not the solution, but pure water.

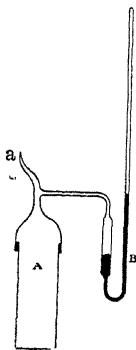


FIG. 27

To complete the apparatus and make an *osmotic cell*, it is only necessary to connect the prepared cell by means of tight joints with a manometer on which the pressure is registered (*Pfeffer*, 'Osmotische Untersuchungen,' Leipzig, 1877).

*Adie* has somewhat modified the method. His apparatus is shown in fig. 27. The upper part is of glass, and is fixed on to a porous cell about 3 inches high and 1 inch internal diameter by means of sealing wax.

*Adie* produces the precipitate in the wall by dipping the cell (clean and dry) into a solution of copper sulphate, and at the same time filling up with a solution of potassium ferrocyanide. The whole, that is, the bath of copper

sulphate solution containing the cell filled with ferrocyanide solution, is placed under the exhausted receiver of an air-pump for two or three days. The air is thus drawn from the pores of the cell, and the semipermeable wall is formed. The semipermeable walls prepared in this way become sufficiently dense to withstand a pressure of from four to four and a half atmospheres (25 to 30 per cent. of the apparatus thus made are good). By long and continued washing the cell is then thoroughly cleaned, and the manometer B is sealed on.

The following *osmotic experiments* can be made with this apparatus.

. After the apparatus has been set up, the cell is filled with a 1 per cent. solution of sugar, then the tube *a* is drawn out and sealed before the blowpipe (an operation which requires a little practice, but after all is not difficult). The apparatus is then immersed in distilled water. The water will penetrate into the cell, and there produce an increased pressure which will be indicated by the manometer. In the course of a few days (or weeks) the maximum pressure will be reached and remain constant for a considerable time. \* This pressure is subject to the following laws:

1. It is proportional to the concentration of the solution employed. This corresponds to *Boyle's law*. At a temperature of 15°

a 1 per cent. solution of sugar gives a pressure of 53.5 cm. of mercury.

. a 2 per cent. solution of sugar gives a pressure of 101.6 cm. of mercury.

a 4 per cent. solution of sugar gives a pressure of 208.2 cm. of mercury.

2. The pressure increases with the temperature according to the equation,

$$p_t = p_0 (1 + \alpha t),$$

where  $\alpha = \frac{1}{273} = 0.00367$ . This corresponds to *Gay-*

Thus, a sugar solution giving at  $14^{\circ}$  a pressure of 51 cm. of mercury, gave at  $32^{\circ}$  a pressure of 54.4 cm.

The perfect analogy between osmotic pressure and the pressure of a gas can be shown in a still more convincing manner. One gram-molecule of a gas gives 84,685 as the value of the constant  $R$  in the equation

$$pv = RT$$

as has already been pointed out (page 38).

In order to form a similar equation for the osmotic pressure, we may consider a 1 per cent. solution of sugar in water at the temperature  $0^{\circ}\text{C}$ . ( $273^{\circ}$  absolute). The volume occupied by a gram-molecule of sugar is then  $342 \times 100$  or 34,200 cubic centimetres. Since the osmotic pressure experimentally found amounts to 49.3 cm. of mercury, *i.e.*  $49.3 \times 13.59 = 671$  grams per square centimetre, we may write:

$$pv (= RT) = 671 \times 34,200,$$

and consequently

$$R = \frac{671 \times 34,200}{273} = 84,200.$$

The constant  $R$  has then approximately the same value whether the equation refer to osmotic pressure or gaseous pressure. *van't Hoff* has based the following law on this concordance: *The osmotic pressure of a solution has the same value as the pressure that the dissolved substance would exercise if, at the temperature of the experiment, it were gaseous and occupied a volume equal to that of the solution.*

The value of the constant  $R$  has been found to be constant for a number of substances. It must, however, be remembered that experiments on osmotic pressure are difficult to carry out, and that so far but few chemists have paid practical attention to the subject, and have restricted their investigations to only a few substances (*Pfeffer, Ladenburg, Adie, &c.*) This criticism is not, however, of

great importance, because the osmotic pressure can be mathematically deduced from certain other properties of solutions, easy to determine and known for a large number of substances. The direct measurement of the osmotic pressure is, therefore, not an absolute necessity. Besides, *Tammann*, *De Vries*, and *Pringsheim*, by indirect methods, have confirmed the laws of the osmotic pressure.

The great majority of organic substances (in general, those of a not very pronounced chemical character) behave like sugar. There is, however, a very numerous class of substances which behave quite abnormally: strong acids, strong bases, and salts, or, as they are termed, *electrolytes*. The osmotic pressure developed by solutions of these substances is very much greater than it should be according to *van't Hoff's* law, and in very dilute aqueous solution may even become  $n$  times too large,  $n$  expressing the number of *ions*<sup>1</sup> into which the molecule splits up. For potassium chloride, for instance, the osmotic pressure is nearly double that calculated for unitary molecules of KCl. We shall have occasion to return to these irregularities later and also to offer an explanation; in the meantime it is sufficient to have noticed them.

#### VAPOUR TENSION AND BOILING POINT OF SOLUTIONS

The vapour tension of a solution is lower than that of the pure solvent.

If we denote the tensions by  $f$  (for the solvent) and  $f'$  (for the solution), the difference  $f - f'$  is at all temperatures a constant fraction of  $f$ :

$$f - f' = \frac{1}{r} f,$$

and this difference is proportional to the concentration of the solution.

If, in equal quantities of the same solvent, different

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<sup>1</sup> See the chapter on Electro-chemistry.

substances, in quantities proportional to their respective molecular weights, are dissolved, the solutions obtained have the same vapour tension.

These facts, ascertained experimentally by *Babo* (1848), *Wüllner* (1856), and *Raoult* (1887), might directly lead to theoretical and practical deductions of the greatest importance. But the determination of a vapour tension is a very delicate operation, and it is preferable to simplify the method of working and start out with three other considerations :

1. The boiling point of a solution is higher than that of the pure solvent ;

2. The rise in the boiling point is proportional to the concentration of the solution ;

3. The rise in the boiling point is the same for equimolecular solutions in the same solvent.

The experimental part of the study is now completely changed. We do not determine vapour tensions, but boiling points; and this we can do by comparatively easy and simple operations.

#### *Beckmann's Method*<sup>1</sup>

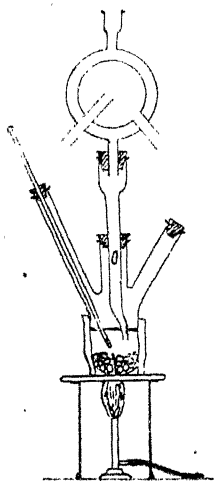


Fig. 28

The apparatus consists of a small flask with three necks and having a short platinum wire sealed into the bottom. The flask rests on an asbestos plate, and is protected from loss of heat by radiation by being bound round with asbestos. One of the side-tubes is used for introducing the solvent and the substance, through the other a Beckmann thermometer passes, and the central one is connected

<sup>1</sup> Only the original form of *Beckmann's* apparatus is here described.—A second form was devised, but is rather complicated,

with a Soxhlet bulb condenser, by means of a special form of adapter.

To carry out an experiment, a sufficiently thick layer of glass beads is put into the flask, then by means of a pipette a weighed quantity of the solvent is introduced. The neck through which the substance is introduced is then closed, and the apparatus heated over a Bunsen burner. Heat is communicated to the liquid through the asbestos plate and along the platinum wire. When the liquid boils, the flame is so regulated that the condenser returns a drop of liquid every five or ten seconds. After about a couple of hours a regular ebullition is established during which the temperature recorded by the thermometer varies only between very narrow limits (a few thousandths of a degree). The boiling point of the solvent is thus obtained.

A weighed quantity<sup>1</sup> of the substance under consideration is then introduced, and after a few minutes, when the thermometer has taken up a new constant position of equilibrium, the temperature is again read off.

Further small weighed quantities of the substance are added and the boiling point after each successive addition noted. In this way, a series of boiling points for more and more concentrated solutions is obtained.

As the whole experiment requires a considerable time, it is well to perform it only on a calm day during which no appreciable variation of the barometric pressure is taking place.

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and would require too long a description.—The latest form (1896) so far resembles the original one that it may be here shortly described. The flask is more cylindrical, and rests on a metal plate covered with asbestos sheet. A small glass cylinder is placed round the flask with the object of reducing radiation to a minimum. The thermometer passes through the central tubulus, and one of the lateral necks is occupied by a very simple form of condenser.

<sup>1</sup> Solid substances are introduced in the form of small lumps or small compressed cylinders. They may also be introduced in the form of powder if enclosed in a piece of platinum gauze of very fine mesh. Liquids are best weighed and introduced by means of a special form of bent pipette.

*Landsberger's Method*

The apparatus resembles that used for a steam distillation and is shown in fig. 27. The vapour from *c*, which passes through *A*, does not pass off at *b* until it has come through the small opening *a* and filled the space between *A* and *B*.<sup>1</sup> The boiling point of the *solvent* is determined as follows: In the tube *A* is placed such a quantity of the liquid that at the end of the experiment the bulb of the thermometer will be well immersed (7 c.c. of ether or carbon

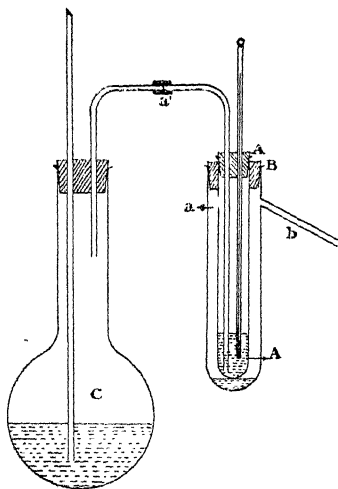


FIG. 29

disulphide, 4 c.c. of chloroform or acetone, 5 c.c. of alcohol, 7 c.c. of water, 0 c.c. of benzene). A sufficient quantity (250 c.c.) of the same liquid is put into the flask *c*. The connections are all made and a Liebig condenser is fitted on to *b*, then the liquid in *c* is boiled and the flame so regulated that the vapour at first condenses in *A*, and afterwards raises the liquid in *A* to its boiling point. After a few (2 to 6) minutes the temperature becomes quite constant, and the boiling point of the solvent may be noted.

The method adopted for obtaining the boiling points of a series of solutions is the following: The tube *A* is dried and weighed (correct to centigrams);<sup>2</sup> then a weighed quantity of the substance and a convenient quantity of the solvent are introduced. The boiling point is then determined just

<sup>1</sup> The tube *A* has a diameter of 3 cm., and is about 16 cm. high.

<sup>2</sup> *A* is weighed along with the cork, bent tube, and thermometer.

as before, and as soon as the thermometer has become stationary the tube A is taken away (*a* and *a'* being at the same time closed with small corks) and after drying is again weighed correct to centigrams. The weight of A and substance subtracted from the weight of A and solution gives the weight of the solvent. *Walker and Lumsden*<sup>1</sup> have modified this method, so that the volume, and not the weight of the solvent, is observed. *Landsberger's* method has the advantage of greater rapidity over *Beckmann's*. The thermometer employed must be very sensitive and graduated in twentieths of a degree. *Landsberger* recommends the use of a series of thermometers, each of which has a scale about 20 cm. long and registering only about ten degrees.

*Remark.*—For the application of these methods, the substance must not distil with the vapour of the solvent. Its boiling point must, therefore, be higher, by at least 130 degrees, than that of the solvent.

*Theoretical Deductions.*—The two methods lead to the same result. They both show us that a solution whose composition corresponds to *p* grams of substance in 100 grams of solvent boils *t*° higher than the solvent. Accepting the principles which are given at the beginning of this chapter, we may reason as follows: If in the 100 grams of solvent we had put *p* times less substance, that is, if we had made a 1 per cent. solution, the rise in the boiling point would have been  $\frac{t}{p}$  degrees; and if we had dissolved one gram-molecule the elevation would have been  $\frac{t}{p}$  M degrees (where M is the molecular weight). We thus calculate the molecular elevation of the boiling point, E, which is independent of the nature of the dissolved substance, and varies only with the solvent employed.

For any given solvent we can ascertain E by two means:

<sup>1</sup> *Journ. Chem. Soc.*, 73, 502 (1898).—Tr.



(1) We can dissolve a substance of well-known molecular weight in it, and determine a series of correlative values of  $t$  and  $p$ , then apply the equation  $\frac{t}{p} M = E$ ;

or (2) We can derive the value of  $E$  by making use of the relationship established by *van't Hoff*, which is expressed by the equation (to be gone into more fully later):

$$E = \frac{0.02 T^2}{l}$$

where  $l$  is the latent heat of vaporisation of one gram of the solvent and  $T$  is its boiling point on the absolute scale.

The following are some of the values found for  $E$ , the boiling point being also given :

	Boiling point (Centigrade)	$E$
<i>Ethyl ether</i> . . . . .	35°	21.6
<i>Acetone</i> . . . . .	56°	17.1
<i>Methyl alcohol</i> . . . . .	66°	8.8
<i>Ethyl alcohol</i> . . . . .	78°	11.7
<i>Water</i> . . . . .	100°	5.2
<i>Acetic acid</i> . . . . .	118°	25.3
<i>Phenol</i> . . . . .	183°	30.4
<i>Carbon disulphide</i> . . . . .	46°	23.5
<i>Carbon tetrachloride</i> . . . . .	76°	43.0
<i>Benzene</i> . . . . .	80.3°	26.7

*Practical Application.*—When once we are in possession of this table, we can follow the reverse process, and by means of the rise in the boiling point determine the molecular weight of a dissolved substance.

From the knowledge simply of  $p$  and  $t$  of a single solution, the value of  $M$  can be calculated from the equation  $M = E \frac{p}{t}$ . But, in practice, it is necessary to examine

a series of solutions of different concentrations, and from the observed correlative values of  $p$  and  $t$ ,  $M$  is calculated, and a graphic curve (something like the one shown in fig. 30) of the values obtained is drawn.

The curve  $m$   $m'$  generally approaches a line parallel with the abscissæ. But in certain cases (such as phenanthrene in benzene solution) the values found from the more concentrated solutions are too high, corresponding to an association of the molecules. In the more dilute solutions, this anomaly is not so marked, and from the course of the curve we can see what the (true) molecular weight would be at infinite dilution.

This irregularity occurs most often when we make use of the last three solvents mentioned in the list, and more especially with benzene. The first seven solvents on the list, on the contrary, have a dissociating action, and it is only in very rare cases that polymerised molecules can remain dissolved in them.

*Remark.* — Electrolytes, which form the exception to van't Hoff's osmotic pressure law, behave, in respect to the raising of the boiling point, also in an abnormal manner.

In aqueous solution the molecular weight found for them by this method is only a fraction of the real value. Thus, for sodium chloride of molecular weight 58.5, the boiling-point method with a dilute solution of the salt gives only about 29.2.

As before, this difficulty can only be explained after we have learned some more about salt solutions.

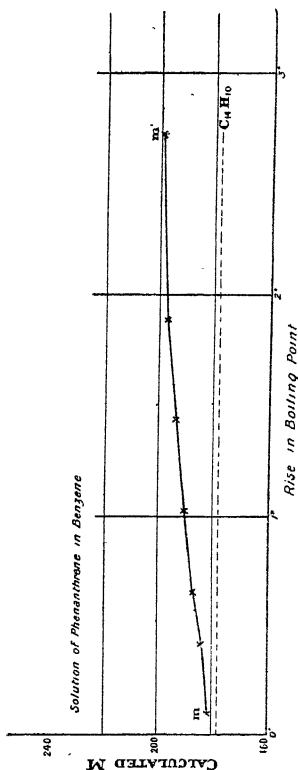


FIG. 30

## FREEZING POINT OF SOLUTIONS (CRYOSCOPY)

(Blagden, 1788 ; Rüdorff, 1861 ; de Coppet, 1871 ;  
Raoult, 1882)

When a dilute solution freezes,<sup>1</sup> the solid matter which is at first deposited is almost always pure solvent;<sup>2</sup> and pure solvent continues to be separated as long as the remaining liquid solvent is capable of retaining the dissolved substance in solution.

The laws which obtain for the freezing points resemble those which govern the boiling points :

The freezing point of a solution is lower than that of the pure solvent ;

The depression of the freezing point is proportional to the concentration of the solution ;

The depression is the same for equimolecular solutions in the same solvent.

*Beckmann's method* is the one usually adopted for the determination of the freezing point of a liquid.

The apparatus consists essentially of two test-tubes, one within the other, so as to leave an air-space between the two, which acts as a bad conductor of heat. A very sensitive thermometer, graduated in hundredths of a degree, and a platinum stirrer, complete the apparatus (fig. 31).

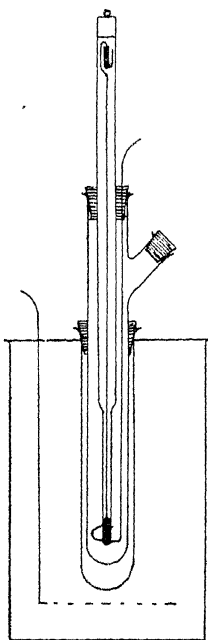


FIG. 31

<sup>1</sup> The term 'freeze' is here used in a general sense: water freezes at 0°, naphthalene freezes or solidifies at 79°.

<sup>2</sup> When the solvent and the dissolved substance are isomorphous or of very similar chemical character, sometimes the solid separated on freezing is a mixture of the two (a 'solid solution'). This is the

When the apparatus has been submerged in a suitable freezing mixture (the temperature of which should be one or two degrees below the expected freezing point) a certain quantity of the liquid to be examined is introduced into the inner tube, and is gently stirred. The liquid is cooled, but remains in a supercooled state a few tenths of a degree below its freezing point. Partial solidification is then suddenly induced, either by vigorous agitation, or by dropping in a small particle of previously solidified solvent.

The latent heat of solidification soon causes the thermometer to rise to the proper freezing point of the liquid. Any excess of heat would not affect the thermometer, because it would be used up in fusing a part of the solidified substance.

This determination being made for the pure solvent, the freezing points of a series of solutions of different concentrations are next determined.

*Remarks.*—The substance to be dissolved is added in the same way as directed in the footnote in the preceding chapter.

In using certain hygroscopic solvents, such as acetic acid and phenol, precaution must be taken to avoid their coming in contact with the atmosphere.<sup>1</sup>

The temperature of the cooling bath should be only one or two degrees below the freezing point of the solution, and should be kept as constant as possible during the whole of the experiment.

*The Theoretical Deductions* are absolutely the same as those of the preceding chapter. If  $t$  degrees be the depression produced by the presence of  $p$  grams of substance in

---

case for a solution of thiophene, pyrrol, piperidine, or quinoline in benzene; and for a solution of indol, quinoline, or  $\beta$ -naphthol in naphthalene.

<sup>1</sup> When working with such a solvent it is advisable to aspirate a current of dry air through the upper part of the inner tube. This can be done by allowing the air to enter by the lateral tube, and pass off through a narrow tube through which the stirrer goes.

100 grams of solvent, then the molecular depression  $c$  will be  $\frac{t}{p} M$ , where  $M$  is the molecular weight of the dissolved substance.

The value of  $c$  is independent of the nature of the substance dissolved, and varies only with the solvent employed.

For any given solvent, there are two methods of ascertaining the value of  $c$ .

(1) We may determine the depression caused by the solution of a certain weight of a substance of known molecular weight in a certain amount of the solvent, and calculate  $c$  from the equation

$$c = \frac{t}{p} M$$

or (2) We may find  $c$  from *van't Hoff's* formula : <sup>1</sup>

$$c = \frac{0.02 T^2}{\lambda},$$

in which  $T$  is the freezing point (in absolute degrees), and  $\lambda$  is the latent heat of fusion of one gram of the solvent.

The following table gives the values of  $c$  (experimental and calculated by *van't Hoff's* formula) and of  $T$  and  $\lambda$ .

—	C experi- mental	C calcu- lated	T abso- lute	$\lambda$
Water . . .	18.5	18.8	273°	79.4 calories (small)
Acetic acid . .	38.6	39.7	289.7	42.4    "
Phenol . . .	74	74	313	25    "
Formic acid . .	27.7		281.5	
Ethylene bromide	118		282	
Benzene . . .	50	52.4	278	29.5    "
Naphthalene . .	69	69	352	36    "
Nitro-benzene . .	70.7	69.2	276	22    "

<sup>1</sup> In his calculations *van't Hoff* denotes by  $p$  the weight of substance dissolved in  $(100 - p)$  grams of solvent or 100 grams of solution. For dilute solutions the difference between this and *Raoult's* system is very small.

*Application.*—When the value of  $c$  has been determined, cryoscopic experiments can be made in order to find the molecular weight of a substance. The determination of the freezing point of a single solution of the substance, and calculation from the equation :

$$M = c \frac{p}{t}$$

should theoretically be sufficient. But, in practice, it is absolutely necessary to calculate  $M$  from a series of observations on solutions of different concentrations and make a graphic curve of the values obtained, marking off the depressions on the abscissæ-axis and the values of  $M$  on the ordinate. The curve generally shows that the most satisfactory results are those obtained from very dilute solutions. Concentrated solutions may contain the substance in a more or less associated state and thus lead to much too high values for the molecular weight.

The most abnormal values are obtained for substances containing one or more hydroxyl groups (alcohols, organic acids, phenols, oximes, and also amides) in certain solvents possessing an associating power such as benzene, naphthalene, and nitro-benzene.

*Important Remark.*—Those substances which we have already noticed as exceptions at the end of the last two chapters behave here also in an abnormal manner: Electrolytes, in aqueous solution, always yield much too low results for the molecular weight by the cryoscopic method. It is to be noted, however, that amongst the electrolytes we must not class certain acids and bases whose aqueous solutions are poor conductors of an electric current and which give a normal depression of the freezing point. Sulphurous acid, hydrogen sulphide, and ammonia belong to this category.

•

## THE BECKMANN THERMOMETER

In boiling point and cryoscopic determinations the thermometer used is generally of the pattern devised by *Beckmann*. This instrument consists of a very fine capillary tube terminating in two mercury reservoirs. The lower reservoir is comparatively large and corresponds to the bulb of an ordinary thermometer. The upper one is constructed as shown in fig. 32, and contains an auxiliary quantity of mercury.

The scale extends only over five or six degrees, each divided into hundredths, but the mercury column can be so adjusted that it terminates at a convenient part of the scale at any desired temperature.

Suppose that a cryoscopic determination has to be made in acetic acid, that is, about the temperature  $16^{\circ}\text{C}$ . To adjust the thermometer to this temperature, it is placed in a bath and heated until the mercury column rises and joins the mercury in the upper reservoir. It is then placed in a second bath whose temperature, indicated by an ordinary thermometer, is about  $18^{\circ}$  or  $19^{\circ}$ . When this temperature is reached, the upper reservoir is tapped with



FIG. 32.

the hand and the mercury thread is broken at the point marked *a* in the figure. Further cooling to about  $16^{\circ}$  brings the end of the mercury column to a convenient position opposite the graduated scale.

The same thermometer can be used at various temperatures— $0^{\circ}$ ,  $16^{\circ}$ ,  $100^{\circ}$ , &c. For very exact measurements it is best to consider the divisions on the scale as arbitrary and to ascertain the value of the degree at the time, by comparison with a reliable standard thermometer. We may also obtain sufficiently accurate results by making use

of the following table of corrections by *Grützmacher* and multiplying the *increase* in the boiling point or the *depression* of the freezing point by the given factor :

Temperature			Factor
about	- 35° to - 30°	...	0.977
„	0° to 5°	...	0.995
„	45° to 50°	...	1.015
„	95° to 100°	...	1.032
„	145° to 150°	...	1.045
„	195° to 200°	...	1.053
„	245° to 250°	...	1.055

## THEORETICAL RELATIONS

• A. *The Osmotic Pressure of a solution and its Vapour Tension* (*Arrhénius*).

Let us imagine a vessel of the form of a tube terminated at the lower end by a funnel which is closed by a semipermeable wall, as shown in fig. 83. Let this vessel be filled with a solution *s* and stand in another vessel containing pure solvent *D*. Let the whole be covered with a bell-jar and completely exhausted.

• Equilibrium will be established when the osmotic pressure has forced the solution to a height *h*, and the free space in the bell-jar is saturated by the vapour *D'*.

At the surface *h* the vapour given out by the solution has a tension *f'*, and at the same height the vapour given out by the solvent has a tension (*f* - *hd*), *h* being the height of the liquid column from the surface *D*, and *d* the density of the vapour in the bell-jar. We say then that equilibrium exists when

$$f' = (f - hd)$$

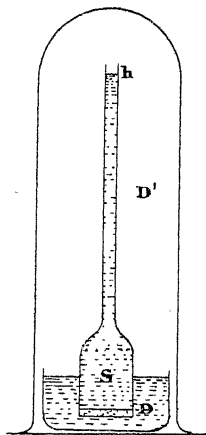


FIG. 33

Because, if *f'* were smaller than (*f* - *hd*), the following would occur. The vapour given out from *D* would condense at *h*, and would there be deposited as liquid which would increase the weight of the osmotic column and would dilute the solution. The equilibrium being thus broken, a certain quantity of *solvent* would be forced through the



semipermeable wall, which would compensate for the loss by evaporation suffered by D. The state of affairs would then be exactly as before, and the same process would commence again and go on indefinitely; we should thus have a case of perpetual motion, which is impossible.

By analogous reasoning, it can be shown that  $f'$  cannot be greater than  $(f - hd)$ ; hence we conclude that

$$f' = (f - hd).$$

Let us now suppose that  $s$  is a *very dilute solution containing  $n$  gram-molecules of dissolved substance in  $g$  grams of solvent*; and let us accept the equality which we have just established. We can then express  $h$  and  $d$  in terms of  $n$ ,  $g$ ,  $M$  (molecular weight (gaseous) of the solvent),  $f$  and  $RT$ .

*Calculation of  $h$ .*—If we assume *van't Hoff's law* on osmotic pressure and denote by

$p$ , the osmotic pressure;

$v$ , the volume of the solution;

and  $s$  the specific gravity of the solution, as also of the solvent (which is permissible for very dilute solutions);

$$\text{we have} \quad pv = RT \times n$$

$$\text{But} \quad p = h \times s,$$

$$\text{and} \quad v = \frac{g}{s}.$$

$$\text{Therefore,} \quad pv = (nRT) = hs \times \frac{g}{s} = hg,$$

and consequently,

$$h = \frac{nRT}{g}.$$

*Calculation of  $d$ .*—One gram-molecule of the vapour emitted from D would occupy a volume which we shall denote by  $v$ , and the pressure of this vapour is  $f$ .<sup>1</sup> According to the general gas equation, we have, therefore:  $fv = RT$ ,

$$\text{and} \quad v = \frac{RT}{f}.$$

$$\text{Now} \quad d = \frac{M}{v}.$$

$$\text{Therefore,} \quad d = \frac{Mf}{RT}.$$

---

<sup>1</sup> Since we are working with a very dilute solution the height  $h$  is small, and to express the pressure of the vapour which fills the bell-jar we may take either  $f$  or  $f'$ , or the mean of these two.

If now we introduce these values of  $h$  and  $d$  into the original equation, we transform it into :

$$f' = f - \frac{nRT}{g} \times \frac{f}{RT} = f - \frac{nMf}{g},$$

and 
$$\frac{f - f'}{f} = M \frac{n}{g}.$$

*Remark.*—Such is the strict conclusion of our reasoning. Some chemists, however, have gone further, and put

$$\frac{f - f'}{f} = \frac{n}{\frac{g}{M}} = \frac{n}{N}.$$

The last term of the equation then simply expresses the relation between the number of dissolved molecules and the number of solvent molecules. But this transformation presupposes that the solvent has the same molecular size in the gaseous and in the liquid states, a condition which in most cases, notably for water, is not fulfilled.

#### B. Osmotic Pressure and Boiling Point.

Let us still consider a very dilute solution containing  $n$  molecules dissolved in  $g$  grams of solvent.

Let  $\Delta$  be the rise in the boiling point, then dividing by  $n$ , we find what the rise would be for one molecule dissolved, and multiplying then by  $g$ , we find what it would be for one molecule dissolved in one gram.

For a given solvent  $\Delta \frac{g}{n} = \pi'$  must be constant, and it is to be noticed that this constant refers to one molecule of substance dissolved in one gram of the solvent.

*Thermodynamical calculation of the constant  $\pi'$  (van't Hoff).* Suppose we introduce a very large quantity of the solution into an osmotic cell fitted with a tube in which a piston slides. Now, at the absolute temperature  $\tau$ , the boiling point of the solvent, suppose a pressure to be exerted on the piston just sufficient to overcome the osmotic pressure, and suppose that the quantity of solvent forced through the semipermeable wall corresponds to one gram-molecule of dissolved substance. The volume  $v$  thus expelled is the volume of  $\frac{g}{n}$  grams of solvent. If the osmotic pressure which had to be overcome is  $\pi$ , then the work done on the piston is  $\pi v = \pi \tau$ . The liquid which is forced through is then vaporised, and this operation gives  $\frac{g}{n}$  grams of vapour and requires  $\frac{g}{n} l$  calories,  $l$  being the latent

semipermeable wall, which would compensate for the loss by evaporation suffered by D. The state of affairs would then be exactly as before, and the same process would commence again and go on indefinitely; we should thus have a case of perpetual motion, which is impossible.

By analogous reasoning, it can be shown that  $f'$  cannot be greater than  $(f - hd)$ ; hence we conclude that

$$f' = (f - hd).$$

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*Calculation of  $h$ .*—If we assume van't Hoff's law on osmotic pressure and denote by

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$v$ , the volume of the solution;

and  $s$  the specific gravity of the solution, as also of the solvent (which is permissible for very dilute solutions);

we have

$$pv = RT \times n$$

But

$$p = h \times s,$$

and

$$v = \frac{g}{s}.$$

Therefore,

$$pv = (nRT) = hs \times \frac{g}{s} = hg,$$

and consequently,

$$h = \frac{nRT}{g}.$$

*Calculation of  $d$ .*—One gram-molecule of the vapour emitted from D would occupy a volume which we shall denote by  $v$ , and the pressure of this vapour is  $f$ .<sup>1</sup> According to the general gas equation, we have, therefore:  $fv = RT$ ,

and

$$v = \frac{RT}{f}.$$

Now

$$d = \frac{M}{v}.$$

Therefore,

$$d = \frac{Mf}{RT}.$$

<sup>1</sup> Since we are working with a very dilute solution the height  $h$  is small, and to express the pressure of the vapour which fills the bell-jar we may take either  $f$  or  $f'$ , or the mean of these two.

If now we introduce these values of  $h$  and  $d$  into the original equation, we transform it into :

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The last term of the equation then simply expresses the relation between the number of dissolved molecules and the number of solvent molecules. But this transformation presupposes that the solvent has the same molecular size in the gaseous and in the liquid states, a condition which in most cases, notably for water, is not fulfilled.

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For a given solvent  $\Delta \frac{g}{n} = E'$  must be constant, and it is to be noticed that this constant refers to one molecule of substance dissolved in one gram of the solvent.

*Thermodynamical calculation of the constant  $E'$  (van't Hoff).* Suppose we introduce a very large quantity of the solution into an osmotic cell fitted with a tube in which a piston slides. Now, at the absolute temperature  $T$ , the boiling point of the solvent, suppose a pressure to be exerted on the piston just sufficient to overcome the osmotic pressure, and suppose that the quantity of solvent forced through the semipermeable wall corresponds to one gram-molecule of dissolved substance. The volume  $v$  thus expelled is the volume of  $\frac{g}{n}$  grams of solvent. If the osmotic pressure which had to be overcome is  $p$ , then the work done on the piston is  $p v = \pi T$ . The liquid which is forced through is then vaporised, and this operation gives  $\frac{g}{n}$  grams of vapour and requires  $\frac{g}{n} l$  calories,  $l$  being the latent

heat of vaporisation of one gram of the liquid. *The whole system is then raised to the temperature  $(\tau + \Delta)^\circ$ , the boiling point of the solution, and the  $\frac{g}{n}$  grams of vapour are allowed to condense in the solution: the heat of vaporisation formerly dissipated at  $\tau^\circ$  is thus regained at the slightly higher temperature  $(\tau + \Delta)^\circ$ . The whole system is finally cooled to  $\tau^\circ$  and thus brought back to its initial state.*

This cycle may be carried out so that it is reversible, and leads to the equation:

$$\frac{R T}{\frac{g}{n} l} = \frac{\Delta}{T}.$$

Therefore,

$$\Delta = \frac{R T^2}{l} \cdot \frac{n}{g}.$$

But

$$\Delta = E' \frac{n}{g},$$

consequently.

$$E' = \frac{R T^2}{l}$$

In the thermodynamical equation  $R$  represents a quantity of heat, and we have already seen that its value is 2 small calories; therefore, we write

$$E' = \frac{2 T^2}{l}$$

*Remark.*—We have arranged in this equation that  $E'$  refers to one molecule of dissolved substance in one gram of solvent.

In the chapter on Boiling Points we made use of the constant  $E$  which referred to one molecule of substance in 100 grams of solvent, and, consequently, is 100 times smaller than  $E'$ , that is,  $E = \frac{0.02 T^2}{l}$ .

### C. Osmotic Pressure and Cryoscopy

Here also we shall use a very dilute solution containing  $n$  molecules of substance dissolved in  $g$  grams of solvent. In this case  $\tau$  denotes the temperature (absolute) at which the solvent freezes. The solution commences to freeze at the temperature  $(\tau - \Delta)^\circ$ . The cryoscopic constant  $c'$  refers to a solution of one molecule of substance in one gram of solvent, and  $c' = \frac{\Delta g}{n}$ .

*Thermodynamical calculation of the constant  $c'$  (van't Hoff).* In an osmotic cell, fitted as described under calculation of  $E'$ , we put a large quantity of the solution. At the temperature  $\tau^\circ$  a quantity

of the solvent corresponding to one gram-molecule of dissolved substance is expelled through the semipermeable wall, and this requires a work to be done equal to  $\pi r$ . The liquid forced out is then frozen, and thus the system is deprived of  $\frac{g}{n} \lambda$  calories ( $\lambda$  being the latent heat of fusion of one gram of solvent). *The temperature of the solution is then lowered to  $(\tau - \Delta)^\circ$  and the  $\frac{g}{n}$  grams of frozen solvent dropped into it and made to fuse by furnishing the necessary heat. The heat of fusion formerly taken from the system, is thus given back to it, but at a lower temperature. The temperature of the system is then raised to  $\tau^\circ$  and the initial state thus re-established.*

Here, again, we have a reversible cycle which leads to the equation :

$$\frac{\frac{R T}{g} \lambda}{n} = \frac{\Delta}{T}$$

From which

$$\Delta = \frac{R T^2}{\lambda} \cdot \frac{n}{g}$$

But

$$\Delta = c' \cdot \frac{n}{g}$$

Therefore

$$c' = \frac{R T^2}{\lambda},$$

or, substituting 2 for  $R$  as before,  $c' = \frac{2 T^2}{\lambda}$ .

*Remark.*—In the chapter on Cryoscopy we made use of the constant  $c$ . As this refers to one molecule of substance dissolved in 100 grams of solvent, it is 100 times smaller than  $c'$  and, consequently,  $c = \frac{0.02 T^2}{\lambda}$ .

*D. Caution.*—By combining the relationships found under  $\Delta$ ,  $\pi$ , and  $c$ , we can find some very interesting connections between  $f$ ,  $f'$ ,  $\pi$ ,  $\pi'$ ,  $g$ ,  $\Delta$  (for boiling or freezing point),  $\tau$  and  $s$  (also for boiling or freezing point). But these deductions are only exact for extremely dilute solutions whose densities can, without appreciable error, be set equal to that of the solvent. Experiments can hardly be performed on such dilute solutions, and so we must look for discrepancies between the theory and what is actually found.

## III. THE SOLID STATE.

The more important physical properties of solids are:

- (1) The melting point;
- (2) The density or specific gravity;
- (3) The specific heat;
- (4) The solubility in different solvents
- (5) The crystalline form.

This last-mentioned property is the subject of a special science—crystallography; the fourth belongs to the domain of descriptive chemistry; and the third has already been treated of in connection with *Dulong and Petit's law*. As regards the second it suffices here to recall that the density of the elements, or rather their atomic volume, is the basis of *Lothar Meyer's* periodic classification.

The MELTING POINT of a substance is determined in the following manner (if it melts at a reasonably low temperature, say up to 250 or 300°):

A very small quantity of the substance finely powdered is introduced into a narrow glass tube with very thin walls and closed at the bottom. By means of a small rubber ring<sup>1</sup> the tube is fixed on to a thermometer in such a position that the substance is situated close to the mercury bulb. The thermometer and tube are then heated in a suitable bath (water, sulphuric acid, or paraffin) until the substance just begins to fuse. The temperature at which this takes place is noted.<sup>2</sup> The bath should be provided with a stirrer in order to keep the temperature regular.

In special cases the method has to be considerably modified.

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<sup>1</sup> The rubber ring may be dispensed with, and the tube fixed to the thermometer by capillary attraction.

<sup>2</sup> The temperature read off must be corrected by the formula given in the description of the determination of boiling points.

The methods adopted in the case of substances of high melting point are very different (*V. Meyer, Le Chatelier, Holborn and Wien, and Heycock and Neville*).

The comparison of the melting points of organic substances has led to the discovery of certain regularities, similar to those which have been mentioned for the boiling points. But the laws to which allusion is made are as yet too limited in their application and have only been verified for a small number of groups.

The melting point as a qualitative test is of the greatest importance, and may even give quantitative indications, inasmuch as by it we may control the degree of purity of a substance. It has been found that the presence of a very small amount of impurity often lowers the melting point of a substance very considerably. This is very general for organic substances, and more especially for those belonging to the aromatic series. For instance, pure benzoic acid melts at  $120^{\circ}$ , but the presence of a trace of chlorobenzoic acid or nitrobenzoic acid lowers the melting point by several degrees. *Para*-oxybenzoic acid fuses at  $210^{\circ}$ , and the *meta*- isomer at  $290^{\circ}$ ; but a mixture of equal parts of the two melts at  $143\text{--}152^{\circ}$  (*L. Liebermann*).



## THIRD PART

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### I. THERMO-CHEMISTRY

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#### THE CALORIE

IN physics, the *calorie* is that quantity of heat which raises the temperature of one gram of water from  $0^{\circ}$  to  $1^{\circ}$ .

In practice, it is better to take the calorie as that quantity of heat which is necessary to raise the temperature of one gram of water, at the ordinary laboratory temperature ( $15^{\circ}$  to  $18^{\circ}\text{C.}$ ), through one degree. As the specific heat of water is not absolutely constant, the new unit differs slightly from that first defined.

Specific heat of water (*Bartoli and Stracciati*) :

at $0^{\circ}$	...	...	1.00664	at $20^{\circ}$	...	...	0.99947
„ $15^{\circ}$	...	...	1.00000	„ $25^{\circ}$	...	...	1.00005
„ $18^{\circ}$	...	...	0.99959	„ $30^{\circ}$	...	...	1.00241

In works on thermo-chemistry our unit is denoted by the letter *c* : this is the *small calorie*. In many cases, ~~use~~ is made of a unit 1,000 times greater—the *large calorie* (heat necessary to raise 1 kilogram of water through one degree), which is denoted by the capital *C*. The large calorie agrees better with the exactitude of calorimetric observations than the small calorie. Ostwald, in his work on theoretical chemistry, denotes by *k* the quantity of heat required to raise 1 gram of water from  $0^{\circ}$  to  $100^{\circ}$ . This unit is approximately equal to 100 small calories.

*The Mechanical Equivalent of Heat*<sup>1</sup>

From the work of a number of scientists (*Joule, Mayer, Favre, Hirn*, and others) we know that the large calorie is equal to 423.6 to 427 kilogram-metres of work.<sup>2</sup>

The small calorie is therefore equal to 427 gram-metres, 42,700 gram-centimetres, or

$$42,700 \times 980.96 \text{ ergs.}$$

*Rowland* has recently calculated the relationship :

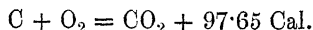
$$\text{at } 15^{\circ} \text{ 1 small calorie} = 41,890,000 \text{ ergs.}$$

$$\text{at } 18^{\circ} \text{ ,, ,, ,, } = 41,880,000 \text{ ergs.}$$

We may take this last figure as the mean equivalent of one small calorie.

*Thermo-chemical Notation*

In thermo-chemistry, the symbols of the elements represent the atomic weight in grams. Thus the equation



expresses that, by the combustion of 12 grams of carbon (amorphous) by 32 grams of oxygen, 97.65 large calories are evolved.

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<sup>1</sup> The principle of the conservation of energy and the idea of the mechanical equivalent of heat are to be found in all physics textbooks, and form part of the scientific training of every student.—The principle, according to which the entropy of a system of bodies tends continually to increase, can only be appreciated from a thermodynamical study. I may, however, here indicate that it is by virtue of this principle that a certain quantity of heat cannot be wholly transformed into mechanical energy; when, in a change of state of a system,  $n$  calories are involved, a certain number ( $x$ ) of these may do a certain mechanical work, but the remainder ( $n-x$ ) is retained in the form of degraded caloric energy (*i.e.* at a lower temperature).

In the same way



indicates, in large calories, the heat of formation of 36.5 grams of gaseous hydrochloric acid.

*Julius Thomsen* has devised a very expressive method of writing thermo-chemical equations. He inserts a comma between the symbols of the reacting substances and encloses them in a bracket.

(H, Cl) = 22.0 C. Heat of formation of gaseous HCl.

(HCl, aq) = 17.4 C. Heat of solution of 36.5 grms. of HCl in much water.

(H, Cl, aq) = 39.4 C. Heat of formation of dissolved HCl.

(H<sup>2</sup>, O) = 58.3 C.; of water in the vapour state.

69.0 C.; of liquid water (about 18°).

70.4 C.; of solid water (at 0°).

(NaOH aq, HCl aq.) = 13.7 C. Heat of neutralisation of caustic soda by hydrochloric acid in dilute solution.

## APPARATUS AND METHODS

### THERMOMETRY

The sensitiveness of a thermometer depends on the relative capacities of the reservoir and the capillary stem.

For calorimetric use the thermometer must be very sensitive and graduated in fiftieths or hundredths of a degree. The exactitude of the instrument is always merely relative, and even the best thermometers require to be provided with a table of corrections. In order to draw up this table, the readings of the thermometer to be corrected may be compared with those of an air-thermometer. Thermometers which have been corrected at official institutes (such as the *Physikalisch-technische Reichsanstalt* at Berlin-Charlottenburg) can now be bought.

The *direct verification* of the zero point is best carried out by the cryoscopic method in Beckmann's apparatus.

The thermometer is fixed in the central tube, which contains a sufficient quantity of pure water. The whole apparatus is cooled a few degrees below zero; then a part of the supercooled water is induced to crystallise. The temperature rises, and the ascension of the mercury stops when the meniscus indicates the true zero.

To verify the  $100^{\circ}$  point, the apparatus shown in fig. 34 is used. The water used must be pure, and nearly the whole thermometer must be suspended in the vapour, the surface of the mercury column extending only a very short distance out of the apparatus. N.B.—The operation will only give an exact indication if it be carried out under a pressure of 760 mm. of mercury. For each millimetre higher or lower than this the boiling point changes by  $\frac{3}{80}$  of a degree. The error at the  $100^{\circ}$  point affects the lower degrees proportionately to their distance from the zero point. Thus at  $75^{\circ}$  the error is 0.75 of that at  $100^{\circ}$ ; at true zero it is nil.

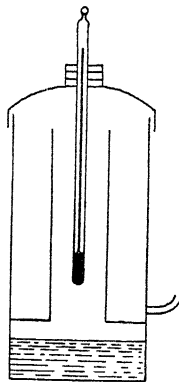


FIG. 34

Let us admit for the present that the points  $0^{\circ}$  and  $100^{\circ}$  on the scale have been found correct. The equidistant marks denoting intermediary temperatures will only be exact if the internal diameter of the capillary is quite uniform. This condition is not generally fulfilled, and by the calibration of the instrument we get a new list of corrections (see *Ostwald's 'Manual of Physico-chemical Measurements,'* English translation by *Walker*).

It is easy to combine all the corrections in one table, or even to give them a graphic representation (correction curve).

The temperatures denoted by a thermometer experimentally corrected do not absolutely agree with those indicated by an instrument which has been graduated

directly or indirectly by comparison with an air-thermometer. The reason for this is to be found in the peculiarities of the relative expansions of mercury and glass.

Whatever be the method of control adopted, it is necessary, in order to *read* the true temperature, to take into consideration the following remarks:

1. When a thermometer has been heated to a rather high temperature (for example, to  $100^{\circ}$ ), the glass does not immediately regain its initial volume. An expanded state is retained such that in melting ice the mercury descends below zero. This residual expansion disappears only slowly (after days or months), so that, if a thermometer is to be used constantly at a high temperature, it is advisable to correct the graduation of the instrument after having maintained it at the temperature in question for about half an hour. (This residual expansion is reduced to a minimum in thermometers made of Jena glass.)

2. The same thermometer in the same medium denotes a slightly different temperature according as the mercury column has come to rest after rising or after falling. This difference tends to disappear if the instrument be gently tapped. To make comparable observations it is necessary always to proceed in the same way, and best to arrange that the mercury reaches its point of equilibrium in rising.

3. To make an exact reading the eye must be brought to the same level as the mercury surface. The so-called parallax error is thus avoided.

### THE CALORIMETER

Thermo-chemical determinations are generally carried out in a water calorimeter by the method of mixture.

The calorimeter consists of a cylindrical vessel of at least 500 c.c. capacity. For smaller dimensions, the surface area becomes relatively very large compared with the volume, and the temperature of the calorimeter is too strongly influenced by that of the surrounding medium.

In order to diminish radiation as much as possible, the surface of the apparatus should be polished. The instrument is set in a polished metallic vessel, and this is supported on badly conducting material in a vessel, which last is set in a bath of water. The outermost vessel is covered with felt. In order to prevent as much as possible loss of heat by evaporation of the water in the calorimeter, the instrument is provided with a cover with holes for the insertion of the thermometer and of a stirrer. This is the *Berthelot* apparatus.

*Julius Thomsen* uses a simpler arrangement. His calorimetric vessel is surrounded by only a single shield made of cardboard or of vulcanite. However, he takes extraordinary precautions to keep the temperature of his laboratory as near  $18^{\circ}\text{C}$ . as possible.

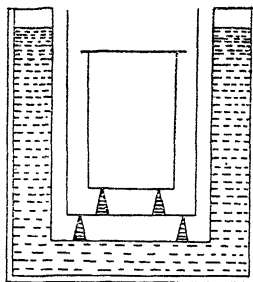


FIG. 35

The calorimeter is preferably made of platinum. This metal resists the action of most chemical reagents, and besides it possesses the advantage of having a very low specific heat. Calorimeters made of nickel, brass, or glass are also much used. Glass is more or less attacked by liquids, and above all has the disadvantage of a high specific heat.

Specific heats :

Platinum . . . . .	0.032
Silver . . . . .	0.057
Nickel . . . . .	0.110
Brass . . . . .	0.094
Glass . . . . .	0.190

Calorimeters are usually provided with a mechanical stirrer, which serves to intimately mix the substances taking part in the action.

In thermo-chemical calculations we have constantly to take into consideration the *water equivalent* of the instruments, or in other terms, their caloric capacity. For the calorimeter, the stirrer, &c., the water equivalent is equal to the weights of these multiplied by their specific heats. The caloric capacity of the thermometer would be difficult to calculate were it not for the favourable circumstance that a cubic centimetre of glass has nearly the same water equivalent as a cubic centimetre of mercury :

$$2.5 \times 0.190 = 0.47 \text{ for glass}$$

$$13.6 \times 0.034 = 0.46 \text{ for mercury.}$$

It is, therefore, sufficient to determine the volume of the immersed part of the thermometer. This volume expressed in cubic centimetres, multiplied by 0.46, gives the water equivalent of the instrument.

*Modus operandi.*—All reactions do not lend themselves to thermo-chemical investigation. This method is only applicable to certain kinds of quick transformations, which are finished after a few minutes, such as the neutralisation of acids by bases in aqueous solution, a large number of double decompositions between salt solutions, certain phenomena of solution, and of dilution, &c. The heat of combustion has been determined for a large number of organic substances and will form the subject of a later chapter.

In order to determine the heat of solution of a substance in the liquid contained in the calorimeter, the substance and the liquid are brought as nearly as possible to the same temperature, then the dissolving process is allowed to take place. By means of the stirrer, an equal distribution of the materials and of heat through the whole mass is attained. The thermometer immersed in the dissolving liquid indicates the changes of temperature.

If it is required to study the action between two liquids or two solutions, one of them is placed in the calorimeter, and the other in a glass flask, or in a platinum

- vessel, furnished at the bottom with a stopcock tube or with a valve. If a flask be used it is placed at the side of the calorimeter; if the metallic reservoir be used it is placed laterally above the calorimeter as shown in fig. 86.

When the temperature of the two liquids has become constant, and is as nearly as possible the same for the one as for the other, they are mixed in the calorimeter—by pouring from the flask or by opening the stopcock or valve of the metallic reservoir. The stirrer is then set in

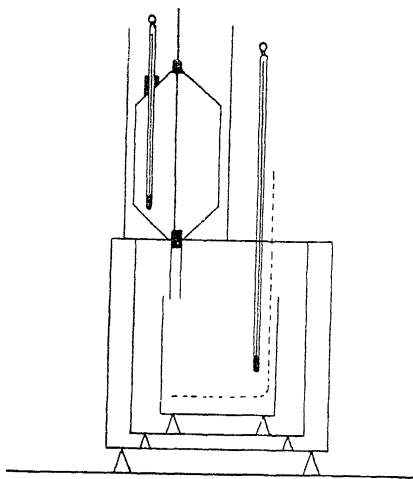


FIG. 86

- motion, and the highest temperature registered by the thermometer is noted. The number of calories evolved in the process is equal to the caloric capacity of the calorimeter and its contents multiplied by the observed change of temperature.

The caloric capacity of the calorimeter is composed of the water equivalent of all those parts of the apparatus which suffer a change of temperature, viz. the calorimeter vessel, the immersed part of the thermometer and of the



stirrer. The caloric capacity of the reacting materials is equal to their weight multiplied by their specific heat. A rigorously exact calculation necessitates therefore a knowledge of these specific heats. In practice, satisfactory results can be obtained (for reactions which take place in very dilute solutions, 1 equivalent of acid or base in 100 or 200 molecules of water), if we assume, as *J. Thomsen* does, that the caloric capacity of a dilute aqueous solution is equal to that of the water which it contains, or if we accept, as *Berthelot* does, that 1 cubic centimetre of each of the liquids is calorimetrically equal to 1 gram of water.

*Example.*—Determination of a HEAT OF NEUTRALISATION. *Thomsen* has studied the action of NaOH (in 100 H<sub>2</sub>O) on HCl (in 100 H<sub>2</sub>O) using a quarter of these quantities.

The solution in the metal reservoir was at the temperature 18.222°. Its water equivalent was 450 grams ( $\frac{1800}{4}$ ).

The solution in the calorimeter was at 18.610°.

Its water equivalent was likewise 450 grams.

The water equivalent of the instrument ~~must be added~~; in this case 13 grams.

After mixing the two solutions the temperature rose to 22.169°. The evolution of heat was, therefore,

$$Q = 450(22.169 - 18.222) + (450 + 13)(22.169 - 18.610) \\ = 1776 + 1648 = 3424 \text{ small calories.}$$

We have now to multiply this number by 4, since only the fourth part of the molecular weights in grams were used.

Therefore, (NaOH aq, HCl aq) = 13.7 C. (large calories).

The example cited is the simplest case which can be met with. The temperature equilibrium (after the reaction) is reached after a very short time, and the thermometer readings can be used directly.

But oftener this equilibrium is only established after several minutes, and then we are not able to observe on

the thermometer the highest temperature which would be attained, since during the operation some heat is lost by radiation. The true maximum temperature can be calculated by many methods which are given in works on thermo-chemistry (especially in *Berthelot's* 'Calorimétrie pratique').

#### REGNAULT-PFAUNDLER'S METHOD OF CORRECTION

Let us suppose that in a calorimetric operation we have observed the temperature after intervals of 20 seconds during the three following periods:

1. Before the reaction. The variations of the surface of the mercury are regular, and sensibly proportional to the interval of time between two observations.

2. During the reaction. The mercury rises rapidly at first, then more slowly until a certain maximum is reached, after which it descends slowly at first, then:

3. The downward progress of the mercury becomes regular, and the variation of the position of the surface again becomes proportional to the time. This indicates the end of the reaction.

Let us suppose that during the first period 10 readings have been taken after intervals of twenty seconds. Let us denote these readings by the letter  $t$  with the interval affixed. By direct observation, we shall know  $t_0, t_1, t_2, t_3, \dots$  up to  $t_9$ . At the moment  $t_{10}$  the reacting substances are mixed, so that we are not able to read this temperature. But we can deduce it from the fact that  $t_{10}$  is equal to  $t_9$  increased by the mean of the changes of temperature observed during the preceding nine intervals. From this we get the equation

$$t_{10} = t_9 + \frac{t_0 - t_9}{9}$$

In the second period (during the reaction), the readings  $t_{11}, t_{12}, \dots$  up to  $t_{20}$  are taken. Here we must assume

that immediately after  $t_{20}$  the descent of the mercury has become regular.

In the third period (after the reaction), the temperatures  $t_{21}, t_{22} \dots t_{30}$  are read off, and from this we find that radiation produces a fall of  $\frac{t_{20} - t_{30}}{10}$  degrees per interval of twenty seconds.

The real maximum temperature is calculated as follows:

Mean temperature of the first period:  $t_5$ .

Mean loss by radiation for each interval of twenty seconds of this period:

$$\Delta_5 = \frac{t_0 - t_{10}}{10}.$$

Mean temperature of the third period:  $t_{25}$ .

Mean loss by radiation during this period:

$$\Delta_{25} = \frac{t_{20} - t_{30}}{10}.$$

We can admit that the losses by radiation which correspond to successive intervals (20'') are proportional (approximately) to the initial temperatures of these intervals. We shall then have

$$\Delta_n : \Delta_5 = t_n : t_5 \quad \text{and} \quad \Delta_{25} : \Delta_5 = t_{25} : t_5,$$

from which we get

$$\frac{\Delta_n - \Delta_5}{\Delta_5} = \frac{t_n - t_5}{t_5} \quad \text{and} \quad \frac{\Delta_{25} - \Delta_5}{\Delta_5} = \frac{t_{25} - t_5}{t_5}.$$

Consequently,

$$(\Delta_n - \Delta_5) : (\Delta_{25} - \Delta_5) = (t_n - t_5) : (t_{25} - t_5)$$

and

$$\Delta_n = (t_n - t_5) \frac{\Delta_{25} - \Delta_5}{t_{25} - t_5} + \Delta_5.$$

This equation gives us the cooling corresponding to the successive intervals of the principal period. For the

interval of twenty seconds between the tenth and eleventh readings the loss by radiation will be

$$\Delta_{10-11} = \left( \frac{t_{10} + t_{11}}{2} - t_5 \right) \frac{\Delta_{25} - \Delta_5}{t_{25} - t_5} + \Delta_5.$$

It is to be noticed that for  $t_u$  we take the mean of the temperatures  $t_{10}$  and  $t_{11}$ .

Similarly,

$$\Delta_{11-12} = \left( \frac{t_{11} + t_{12}}{2} - t_5 \right) \frac{\Delta_{25} - \Delta_5}{t_{25} - t_5} + \Delta_5,$$

and so on up to  $\Delta_{19-20}$ .

The sum of all these falls of temperature will be

$$\Sigma\Delta = (t_{11} + t_{12} + \dots + t_{19} + \frac{t_{10} + t_{20}}{2} - 10t_5) \frac{\Delta_{25} - \Delta_5}{t_{25} - t_5} + 10\Delta_5.$$

By adding the number of degrees  $\Sigma\Delta$  to the last temperature observed in the second period we obtain the corrected maximum temperature :

$$t_{20} + \Sigma\Delta.$$

## CHEMICAL AFFINITY AND CALORIMETRY :

### *First Fundamental Principle*

In a compound composed of the atoms  $a$  and  $b$ , these are disposed at a fixed distance from each other. Suppose that the molecule  $ab$  meets another  $cd$  under circumstances which favour a double exchange, and that in the new compounds  $ad$  and  $bc$  the atoms are more closely united than they were in the initial molecules. On coming together, the atoms will have traversed a path under the influence of a force of attraction. The system, therefore, will have lost a certain quantity of *potential energy*, which becomes externally manifest in some form. Molecules themselves may, on coming together, contribute to the same phenomenon.

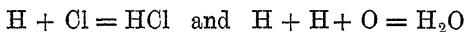
The energy lost by the atoms or molecules may manifest itself in the form of heat, electricity, light, or mechanical motion. *Thermo-chemistry treats of the heat phenomena which accompany chemical reactions.*

From what has been said it would seem, *a priori*, that THE THERMAL EFFECT OF A REACTION GIVES US A MEASURE OF THE AFFINITIES OF WHICH IT IS THE RESULT. And particularly, the heat of formation of a compound from its elements would be proportional to the affinities which unite the atoms.

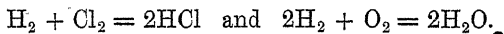
In fact, if in a reaction the atoms rearrange themselves so as to enter into new unions, the amount of chemical energy transformed into heat will be the greater according as the new attractions entering into play are greater than the old attractions.

It is necessary, however, to notice that the changes which take place in the relationship between the *molecules*—that is to say, in the physical state of the matter, the density, the cohesion, the crystalline form, &c.—give rise to thermal effects which are generally very considerable. As yet, we have not succeeded in determining what part of the general thermal effect (calories in a thermo-chemical observation) is due solely to the influence of the atomic affinities, and what part is due to the changes in the state of the molecules.

Furthermore, even in the case of direct combinations the heat evolved by the union of the isolated atoms is absolutely unknown. In the direct formation of hydrochloric acid gas from hydrogen and chlorine, or in the synthesis of water from its elements, the equations



are not realised, but true double decompositions take place,



The true heat of formation of two molecules of hydrochloric acid from *isolated* atoms of hydrogen and chlorine

is greater than the thermal effect observed (44 C.) by the sum of that quantity of heat required for the decomposition of one molecule of chlorine and that necessary for the decomposition of one molecule of hydrogen.

Besides, we know that this reaction, although capable of evolving much heat, does not take place when the two elementary gases are mixed. It requires to be started by the action of light or of heat, that is, by the co-operation of external energy, because it is necessary to weaken to a certain extent the force which unites the similar atoms, so that the preponderating attraction between the heterogeneous atoms may overcome this and bring about the change. Combination started at a point quickly propagates itself through the whole mixture, on account of the heat evolved by the reacting particles. Therefore, in the case of direct combination the quantity of heat evolved must be subjected to a correction in order to give a measure of the chemical affinity. We do not know how to make this correction, as we do not know how much heat is dissipated in separating the similar atoms.

The thermo-chemical numbers, therefore, give us only a rough measure of affinities, with an approximation which we cannot estimate. Nevertheless, on reviewing a table of Heats of Formation we at once notice that the most stable compounds, those which we are in the habit of regarding as containing the strongest affinities, are those which have the greatest heat of formation.

## HEATS OF FORMATION (IN LARGE CALORIES)

*Components and products in their natural state at 15°C., unless otherwise indicated.*

		Gaseous	Liquid	Solid	Dis- solved
(H, Cl) . . .		22.0			39.4
	at 2,000° . . .	26.0			
(H, Br) . . .	from liquid Br . .	8.6			28.6
	„ gaseous Br . . .	12.3			32.3
(H, I) . . .	„ solid I . . .	-6.4			13.2
(H, F) . . .		38.5	45.7		50.3
(H <sub>2</sub> , O) . . .		58.3	69.0	70.4	69.0
	at 2,000° . . .	50.6		(at 0°)	
(H <sub>2</sub> , O <sub>2</sub> ) . . .					47.3
(H <sub>2</sub> , S) . . .	from octahedral S .	4.8			9.5
(N, H <sub>3</sub> ) . . .		12.2	16.6		21.0
(N, H <sub>3</sub> , O) . . .				27.6	23.8
(N <sub>3</sub> , H) . . .	(hydrazoic acid) .				55.2
(P, H <sub>3</sub> ) . . .	from yellow P . . .	4.9			
(As, H <sub>3</sub> ) . . .	from crystallised As . . .	-44.2			
(Sb, H <sub>3</sub> ) . . .		-86.8			
(C <sub>2</sub> , H <sub>2</sub> ) . . .	from diamond . . .	-58.1			
(C <sub>2</sub> , H <sub>4</sub> ) . . .		-14.6			
(C <sub>2</sub> , H <sub>6</sub> ) . . .		23.3			
(C, H <sub>4</sub> ) . . .		18.9			
(Si, H <sub>4</sub> ) . . .	from crystalline Si . . .	-6.7			
(O <sub>3</sub> ) ozone . .	from ordinary oxygen . . .	-30.7			
(Cl <sub>2</sub> , O) . . .		-15.1			-5.7
(Cl, O, H) . . .					31.65
(Cl <sub>2</sub> , O, H <sub>2</sub> O) . .					-5.7
(Cl <sub>2</sub> , O <sub>5</sub> , H <sub>2</sub> O) . .					-25.0
(Cl <sub>2</sub> , O <sub>7</sub> , H <sub>2</sub> O) . .					9.2
(Br <sub>2</sub> , O, H <sub>2</sub> O) . .	from liquid Br . .				-10.8
(Br <sub>2</sub> , O <sub>3</sub> , H <sub>2</sub> O) . .					-44.0
(I <sub>2</sub> , O <sub>5</sub> , H <sub>2</sub> O) . .	from solid I . . .				46.4
(I <sub>2</sub> , O <sub>7</sub> , H <sub>2</sub> O) . .					38.0
(S, O <sub>2</sub> ) . . .	from octahedral S .	69.8	74.7		77.6
(S, O <sub>3</sub> ) . . .		92.0		103.8	141.1
(H <sub>2</sub> , S, O <sub>4</sub> ) . . .			192.2	193.1	210.1
(S, O <sub>3</sub> , H <sub>2</sub> O) . .			123.2	124.1	141.1
(H <sub>2</sub> , S <sub>2</sub> , O <sub>3</sub> ) . .					141.7
(H <sub>2</sub> , S <sub>2</sub> , O <sub>8</sub> ) . .	(persulphuric acid) . . .				316.4
(N <sub>2</sub> , O) . . .		-20.6	-18.8		-14.4

HEATS OF FORMATION (IN LARGE CALORIES)—*continued*

		Gaseous	Liquid	Solid	Dis- solved
(N, O) . . .		- 21.6			
(N <sub>2</sub> , O <sub>3</sub> ) . . .		- 21.4			
(N, O <sub>2</sub> , H) . . .					30.3
(N <sub>2</sub> , O <sub>3</sub> , H <sub>2</sub> O) . . .					- 8.4
(N, O <sub>2</sub> ) . . .	at 200° . . .	- 7.9			
(N, O <sub>3</sub> , H) . . .		34.4	41.6	42.2	48.8
(P, O <sub>3</sub> , H <sub>2</sub> ) . . .			225.7	228.9	228.8
(P <sub>2</sub> , O <sub>3</sub> , 3H <sub>2</sub> O) . . .			244.6	250.8	250.6
(P <sub>2</sub> , O <sub>3</sub> ) . . .				365.2	400.9
(P <sub>2</sub> , O <sub>3</sub> , 3H <sub>2</sub> O) . . .			396.1	401.7	406.5
(As <sub>2</sub> , O <sub>3</sub> ) . . .	opaque As <sub>2</sub> O <sub>3</sub> . . .			156.4	148.9
(As <sub>2</sub> , O <sub>5</sub> ) . . .				219.0	225.0
(As <sub>2</sub> , O <sub>5</sub> , 3H <sub>2</sub> O) . . .				225.8	225.0
(Sb <sub>2</sub> , O <sub>3</sub> ) . . .				166.9	
(Bi <sub>2</sub> , O <sub>3</sub> ) . . .				139.2	
(B <sub>2</sub> , O <sub>3</sub> ) . . .	from amorphous B			272.6	279.9
(Si, O <sub>2</sub> , aq) . . .	hydrated silicic acid—from crystallised Si			179.6	
(Sn, O) . . .				70.7	
(Sn, O, aq) . . .	hydrated SnO . . .			67.8	
(Sn, O <sub>2</sub> ) . . .				141.3	
(Sn, O <sub>2</sub> , aq) . . .				138.7	
(C, O) . . .	from diamond . . .	26.1			
(C, O <sub>2</sub> ) . . .	id. . . . .	94.31			99.91
(C, O) . . .	from amorphous C	29.4			
(C, O <sub>2</sub> ) . . .	id. . . . .	97.65			103.25
(S <sub>2</sub> , Cl <sub>2</sub> ) . . .		10.9	17.6		
(S, O, Cl <sub>2</sub> ) . . .		40.9	47.4		
(S, O <sub>2</sub> , Cl <sub>2</sub> ) . . .		82.8	89.9		
(SO <sub>2</sub> , HCl) . . .	from solid SO <sub>2</sub> . . .	1.55	14.35		
(P, Cl <sub>3</sub> ) . . .		69.7	76.6		
(P, Cl <sub>3</sub> ) . . .				109.2	
(P, O, Cl <sub>3</sub> ) . . .			143.9		
(P, Br <sub>3</sub> ) . . .	from liquid Br . . .		44.8		
(As, Cl <sub>3</sub> ) . . .			71.8		
(Sb, Cl <sub>3</sub> ) . . .				91.4	
(Sb, Cl <sub>3</sub> ) . . .			104.9		
(Bi, Cl <sub>3</sub> ) . . .				90.6	
(B, Cl <sub>3</sub> ) . . .	from amorphous B	89.1	93.4		
(B, F <sub>3</sub> ) . . .		234.8			
(BF <sub>3</sub> , HF) . . .					34.8
(Si, Cl <sub>4</sub> ) . . .	from crystallised Si	121.8	128.1		



## HEATS OF FORMATION (IN LARGE CALORIES)

*Components and products in their natural state at 15°C., unless otherwise indicated.*

		Gaseous	Liquid	Solid	Dis- solved
(H, Cl) . .		22.0			39.4
	at 2,000° . .	26.0			
(H, Br) . .	from liquid Br .	8.6			28.6
	„ gaseous Br .	12.3			32.3
(H, I) . .	„ solid I . .	-6.4			13.2
(H, F) . .		38.5	45.7		50.8
(H <sub>2</sub> , O) . .		58.3	69.0	70.4	69.0
	at 2,000° . .	50.6		(at 0°)	
(H <sub>2</sub> , O <sub>2</sub> ) . .					47.3
(H <sub>2</sub> , S) . .	from octahedral S	4.8			9.5
(N, H <sub>3</sub> ) . .		12.2	16.6		21.0
(N, H <sub>3</sub> , O)				27.6	23.8
(N <sub>2</sub> , H <sub>2</sub> ) . .	(hydrazoic acid) .				55.2
(P, H <sub>3</sub> ) . .	from yellow P .	4.9			
(As, H <sub>3</sub> ) . .	from crystallised As	-44.2			
Sb, H <sub>3</sub> ) . .		-86.8			
C <sub>2</sub> , H <sub>2</sub> ) . .	from diamond .	-58.1			
C <sub>2</sub> , H <sub>4</sub> ) . .		-14.6			
C <sub>2</sub> , H <sub>6</sub> ) . .		23.3			
C, H <sub>4</sub> ) . .		18.9			
Si, H <sub>4</sub> ) . .	from crystalline Si	-6.7			
O <sub>3</sub> ) ozone .	from ordinary oxygen	-30.7			
Cl <sub>2</sub> , O) . .		-15.1			-5.7
Cl, O, H) .					31.65
Cl <sub>2</sub> , O, H <sub>2</sub> O) .					-5.7
Cl <sub>2</sub> , O <sub>3</sub> , H <sub>2</sub> O) .					-25.0
Cl <sub>2</sub> , O <sub>7</sub> , H <sub>2</sub> O) .					9.2
Br <sub>2</sub> , O, H <sub>2</sub> O) .	from liquid Br .				-10.8
Br <sub>2</sub> , O <sub>3</sub> , H <sub>2</sub> O) .					-44.0
I <sub>2</sub> , O <sub>3</sub> , H <sub>2</sub> O) .	from solid I . .				46.4
„ O <sub>7</sub> , H <sub>2</sub> O) .					38.0
„ O <sub>2</sub> ) . .	from octahedral S	69.3	74.7		77.6
„ O <sub>3</sub> ) . .		92.0		103.8	141.1
[S <sub>2</sub> , S, O <sub>1</sub> ) .			192.2	193.1	210.1
[O <sub>3</sub> , H <sub>2</sub> O) .			123.2	124.1	141.1
„ O <sub>3</sub> , H <sub>2</sub> O) .					141.7
„ S <sub>2</sub> , O <sub>3</sub> ) . .	(persulphuric acid)				316.4
„ S <sub>2</sub> , O <sub>8</sub> ) . .					
„ O) . .		-20.6	-18.8		-14.4

HEATS OF FORMATION (IN LARGE CALORIES)—*continued*

		Gaseous	Liquid	Solid	Dis- solved
(N, O) . . .		-21.6			
(N <sub>2</sub> , O <sub>3</sub> ) . . .		-21.4			
(N, O <sub>2</sub> , H) . . .					30.3
(N <sub>2</sub> , O <sub>3</sub> , H <sub>2</sub> O) . . .					- 8.4
(N, O <sub>2</sub> ) . . .	at 200° . . .	- 7.9			
(N, O <sub>3</sub> , H) . . .		34.4	41.6	42.2	48.8
(P, O <sub>3</sub> , H <sub>3</sub> ) . . .			225.7	228.9	228.8
(P <sub>2</sub> , O <sub>3</sub> , 3H <sub>2</sub> O) . . .			244.6	250.8	250.6
(P <sub>2</sub> , O <sub>3</sub> ) . . .				365.2	400.9
(P <sub>2</sub> , O <sub>3</sub> , 3H <sub>2</sub> O) . . .			396.1	401.7	406.5
(As <sub>2</sub> , O <sub>3</sub> ) . . .	opaque As <sub>2</sub> O <sub>3</sub> . .			156.4	148.9
(As <sub>2</sub> , O <sub>3</sub> ) . . .				219.0	225.0
(As <sub>2</sub> , O <sub>3</sub> , 3H <sub>2</sub> O) . . .				225.8	225.0
(Sb <sub>2</sub> , O <sub>3</sub> ) . . .				166.9	
(Bi <sub>2</sub> , O <sub>3</sub> ) . . .				139.2	
(B <sub>2</sub> , O <sub>3</sub> ) . . .				272.6	279.9
(Si, O <sub>2</sub> , aq) . . .	hydrated silicic acid—from crystallised Si			179.6	
(Sn, O) . . .				70.7	
(Sn, O, aq) . . .	hydrated SnO . .			67.8	
(Sn, O <sub>2</sub> ) . . .				141.3	
(Sn, O <sub>2</sub> , aq) . . .				138.7	
(C, O) . . .	from diamond . .	26.1			
(C, O <sub>2</sub> ) . . .	id.	94.31			99.91
(C, O) . . .	from amorphous C	29.4			
(C, O <sub>2</sub> ) . . .	id.	97.65			103.25
(S <sub>2</sub> , Cl <sub>2</sub> ) . . .		10.9	17.6		
(S, O, Cl <sub>2</sub> ) . . .		40.9	47.4		
(S, O <sub>2</sub> , Cl <sub>2</sub> ) . . .		82.8	89.9		
(SO <sub>2</sub> , HCl) . . .	from solid SO <sub>2</sub> . .	1.55	14.35		
(P, Cl <sub>3</sub> ) . . .		69.7	76.6		
(P, Cl <sub>3</sub> ) . . .				109.2	
(P, O, Cl <sub>3</sub> ) . . .			143.9		
(P, Br <sub>3</sub> ) . . .	from liquid Br . .		44.8		
(As, Cl <sub>3</sub> ) . . .			71.3		
(Sb, Cl <sub>3</sub> ) . . .				91.4	
(Sb, Cl <sub>3</sub> ) . . .			104.9		
(Bi, Cl <sub>3</sub> ) . . .				90.6	
(B, Cl <sub>3</sub> ) . . .	from amorphous B	89.1	93.4		
(B, F <sub>3</sub> ) . . .		234.8			
(BF <sub>3</sub> , HF) . . .					34.8
(Si, Cl <sub>4</sub> ) . . .	from crystallised Si	121.8	128.1		

HEATS OF FORMATION (IN LARGE CALORIES)—*continued*

		Gaseous	Liquid	Solid	Dis- solved
(Si, F <sub>4</sub> ) . . .		239.8			
(SiF <sub>4</sub> , 2HF, aq)					57.6
(Sn, Cl <sub>2</sub> ) . . .				80.9	81.3
(Sn, Cl <sub>4</sub> ) . . .		122.2	129.8		158.3
(C, Cl <sub>4</sub> ) . . .	from diamond .	68.5	75.7		
(C, O, Cl <sub>2</sub> ) . . .		44.1			
(Sb <sub>2</sub> , S <sub>3</sub> ) . . .				34.4	
(B <sub>2</sub> , S <sub>2</sub> ) . . .				37.9	
	from amorphous B				
(Si, S <sub>2</sub> ) . . .	from crystallised Si			10.4	
(C, S <sub>2</sub> ) . . .	from diamond .	-25.4	-19.0		
(C <sub>2</sub> , N <sub>2</sub> ) . . .	id.	-73.9	-68.5		-67.1
(C, N, H) . . .		-30.5	-24.8		-24.4
(C, N, H, O) . . .	(cyanic acid) .				37.0
(O, N, K, O) . . .				102.5	97.3
(C, N, K, S) . . .				49.8	43.7

The numbers in this table have been obtained by various investigators, and are taken from *Berthelot's* 'Données et lois numériques' (1897).

For certain very important substances, *J. Thomsen* has found heats of formation which do not quite agree with those given by *Berthelot*. According to *Thomsen* :

$$\begin{aligned}
 (\text{H}_2, \text{O}) &= 68.36 \text{ Cal. (for liquid water at } 18^\circ) \\
 (\text{C}, \text{O}) &= 29.0 \text{ Cal.} \\
 (\text{C}, \text{O}_2) &= 96.96 \text{ Cal.}
 \end{aligned}
 \left. \vphantom{\begin{aligned} (\text{H}_2, \text{O}) \\ (\text{C}, \text{O}) \\ (\text{C}, \text{O}_2) \end{aligned}} \right\} \text{ (for amorphous carbon, at } 18^\circ).$$

We may further quote some interesting data relating to water :

Molecular specific heat :

from -20 to 0° (ice)	:	9.0
" 0 to 100° (water)	:	18.4
at 15°	:	18.0
" 130 to 230° (steam)	:	8.65
Molecular heat of fusion at 0°	:	1.43 Cal.
Molecular heat of vaporisation at 0°	:	10.90 "

## HEATS OF FORMATION (15°)

(IN LARGE CALORIES)

Metallic Oxides	Solid	Dissolved	Sulphides	Solid	Dissolved
(K <sub>2</sub> , O) . . .	98·2	165·2	(K <sub>2</sub> , S) . . .	103·5	113·5
(K <sub>2</sub> , O, H <sub>2</sub> O) . .	140·2	165·2			
(K, O, H) . . .	104·6	117·1	(K, S, H) . . .	64·5	65·3
(Na <sub>2</sub> , O) . . .	100·9	155·9	(Na <sub>2</sub> , S) . . .	89·3	104·3
(Na <sub>2</sub> , O, H <sub>2</sub> O) . .	136·4	155·9			
(Na, O, H) . . .	102·7	112·5	(Na, S, H) . . .	50·3	60·7
(Li, O, H) . . .	112·3	118·1			
(Li <sub>2</sub> , O) . . .	141·2	167·2	(Li <sub>2</sub> , S) . . .		115·4
(N, H <sub>3</sub> , aq) . . .		21·0	(N <sub>2</sub> , H <sub>3</sub> , S) . . .		57·7
			(N, H <sub>3</sub> , S, H) . .	40·0	36·7
(Ca, O) . . .	131·5	149·6	(Ca, S) . . .	90·8	97·1
(Ca, O, H <sub>2</sub> O) . .	146·6	149·6			
(Ca, O, H <sub>2</sub> ) . . .	215·6	218·6			
(Sr, O) . . .	131·2	158·4	(Sr, S) . . .	99·3	106·7
(Sr, O, H <sub>2</sub> O) . .	148·3	158·4			
(Ba, O) . . .	$x$	$x + 28·1$	(Ba, S) . . .	$x - 30·9$	$x - 23·6$
(Ba, O, H <sub>2</sub> O) . .	$x + 17·8$	$x + 28·1$			
(BaO, O) . . .	12·1				
(BaO <sub>2</sub> , H <sub>2</sub> O) . .	2·8				
(Mg, O) . . .	143·4		(Mg, S) . . .	79·4	
(Mg, O, aq) . . .	148·8				
(Mn, O) . . .	90·9		(Mn, S) ppt. . .	45·6	
(Mn, O, aq) . . .	95·1				
(Mn <sub>3</sub> , O <sub>4</sub> ) . . .	328·0				
(Mn, O <sub>2</sub> ) . . .	125·3				
(Mn <sub>2</sub> , O <sub>3</sub> , H <sub>2</sub> O) . .		187·1 (?)			
(Cr <sub>2</sub> O <sub>3</sub> hydr., O <sub>3</sub> ) .	16·4	14·5			
(Fe, O) . . .	65·7		(Fe, S) ppt. . .	24·0	
(Fe, O, aq) . . .	68·9				
(Fe <sub>2</sub> , O <sub>3</sub> , aq) . . .	193·1				
(Fe <sub>3</sub> , O <sub>4</sub> ) . . .	270·8				
(Ni, O, aq) . . .	61·5		(Ni, S) ppt. . .	19·5	
(Co, O, aq) . . .	64·1		(Co, S) ppt. . .	21·9	
(Zn, O) . . .	84·8		(Zn, S) ppt. . .	43·0	
(Zn, O, aq) . . .	83·5				
(Cd, O, aq) . . .	66·3		(Cd, S) ppt. . .	34·4	
(Cu <sub>2</sub> , O) . . .	43·8				
(Cu, O) . . .	39·7 <sup>1</sup>		(Cu, S) ppt. . .	10·1	
(Al <sub>2</sub> , O <sub>3</sub> , aq) . . .	393·0				
(Pb, O) . . .	50·8		(Pb, S) ppt. . .	20·3	
(Pb <sub>2</sub> O <sub>3</sub> ) . . .	63·4				

<sup>1</sup> At a low temperature, 37·7.

HEATS OF FORMATION (15°)—*continued*

Metallic Oxides	Solid	Dissolved	Sulphides	Solid	Dis- solved
(Tl <sub>2</sub> , O) . . .	42.8	39.7	(Tl <sub>2</sub> , S) . . .	21.7	
(Tl <sub>2</sub> , O, H <sub>2</sub> O) . .	45.8	39.6			
(Tl <sub>2</sub> , O <sub>3</sub> , aq) . .	87.6				
(Hg <sub>2</sub> , O) ppt. . .	22.2				
(Hg, O) . . .	21.5		(Hg, S) black; ppt. . .	10.6	
			(Hg, S) red . .	10.9	
(Ag <sub>2</sub> , O) . . .	7.0		(Ag <sub>2</sub> , S) ppt. .	3.0	
(Pt, O) . . .	(?) 17.9				
(Pd, O, aq) . . .	21.0				
(Pd, O <sub>2</sub> , aq) . .	29.1				

*Remarks.*—1. When a substance is *endothermic* (formed with absorption of heat) it is not to be assumed that the isolated atoms combine to produce a negative thermal effect.

The equation  $(I, H) = -6.4 \text{ C.}$  is really the expression of a double decomposition:  $I_2 + H_2 = 2HI$ , and signifies that two free atoms of iodine and two free atoms of hydrogen, in forming two molecules of gaseous hydriodic acid, evolve less heat than in forming one molecule of iodine and one molecule of hydrogen.

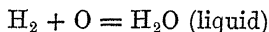
In the same way  $(N_2, O) = -20.6 \text{ C.}$  denotes that in nitrous oxide the atoms are less firmly bound than they are in the elementary gases.

2. In order that thermo-chemical data may have a precise significance, it is necessary that the physico-chemical state of the reacting substances should be well defined. For instance, the heat of combustion is not the same for allotropic modifications of the same element: it is smaller for diamond than for amorphous carbon, also smaller for rhombic sulphur than for the monoclinic or amorphous variety. We see from this that different quantities of heat are dissipated in isolating the *atoms* of sulphur or of carbon from the different modifications of these elements.

3. It is necessary that the thermal influence of all energy external to the system be as far as possible eliminated.

When the combination of two gases under a pressure of 760 millimetres of mercury takes place with contraction, for each molecular volume which disappears there is an evolution of  $(0.54 + 0.002t)$  Cal., due to this contraction. We have seen that one gram-molecule of any gas at normal temperature and pressure occupies a volume of 22,380 cubic centimetres. A contraction of this size corresponds to a pressure of 1,033 grams, exercised by the weight of the atmosphere along a path of 22,380 centimetres, therefore, to a loss of potential energy of  $22,380 \times 1,033$  centimetre-grams, which is equivalent to 0.54 Cal. This quantity of heat, due to an exterior cause, must be deducted from the total thermal effect produced by the reaction.

For instance, in determining the heat of combustion of hydrogen the result differs considerably according as the operation is carried out under constant volume or under constant pressure, that is, in a closed apparatus, or in one the interior of which is in communication with the atmosphere. The heat evolved in the first case is less than that evolved in the second, and the difference between the two is one and a half times 0.54 Cal. (when the calculation is made for the temperature  $0^\circ$ ). In the reaction



there is a contraction of one and a half gaseous molecular volumes.

Theory here has been experimentally confirmed by the work of *Than* and *Thomsen*.

4. The reaction  $\text{H}_2 + \text{Cl}_2 = 2\text{HCl}$  takes place without any change of volume in the gaseous mass. The calorimetric effect would appear then to be due only to the

capacity of its components. The heat evolved by the reaction has, therefore, been augmented by this circumstance and the thermo-chemical data obtained make the affinity action seem larger than it in reality is.

In tables of Heats of Formation we are content with denoting the state of the reacting substances and of the products obtained. Corrections, which would be necessary in order to eliminate the thermal effect caused by change of volume and by variations of the specific heat, are, as a rule, not made.

*Principle of the Initial and Final States*  
(G. H. Hess, 1840)

*The thermal effect of a reaction depends solely on the initial state and final state of the system.* It is the same whatever be the nature and the course of the intermediate stages. It is hardly necessary to mention that all mechanical effects external to the system must be eliminated. In order to clearly see the meaning of this theorem, let us take an example.

If anhydrous lime ( $\text{CaO}$ ) be allowed to react on a dilute solution of hydrochloric acid, a dilute solution of calcium chloride is formed, and 46 Cal. are evolved.

But we can start out from the same initial state and arrive finally at the same dilute solution of calcium chloride by passing through several intermediate states:

The hydration of lime evolves . . . . .	15 Cal.
The solution of the hydrate formed evolves . . . . .	3 "
The reaction (lime-water + dilute HCl solution) evolves	28 "

Adding these together we get 46 Cal., which is the same as in the first operation.

The principle which has just been announced and justified, plays an important rôle in thermo-chemistry, and permits us to acquire some data the direct determination of which would be attended with the greatest difficulty.

The determination of the thermal effect accompanying the change of one allotropic modification of an element into another is based on this principle. The heat of combustion of a certain red phosphorus is less by 20·7 Cal. than that of the yellow modification: the transformation of this latter into the red variety is therefore accompanied by an evolution of 20·7 Cal.<sup>1</sup>

The *heat of hydration of acids, of bases, and of salts*, the difference between the heats of neutralisation of two different acids by the same base, or of two different bases by the same acid, and the *heat of formation of organic compounds* are further examples of this same indirect method. For details the reader is referred to the following chapters.

### Solution

GASES which dissolve in water according to *Henry's law* have a very low heat of solution.

Amongst those gases which do not obey this law, there are some whose solution is attended with a very considerable heat effect, greater even than the heat of liquefaction of the gaseous substance. The difference between these two heats represents the heat evolved by the action of water on the liquefied gas.

Examples (*Berthelot*):

	Heat of Solution (per gram-molecule)	Heat of Liquefaction (per gram-molecule)
Chlorine . . .	3·0 Cal.	
Bromine . . .	8·3 „	7·0 Cal.
Hydrochloric acid	17·4 „	
Hydrobromic „ .	20·0 „	
Hydriodic acid . .	19·6 „	
Ammonia . . .	8·8 „	4·4 Cal.
Carbon dioxide . .	5·6 „	2·5 „, at 0°.
Sulphur dioxide . .	8·3 „	6 „, (about).

The solution was made in much water (100 to 500 molecules)  
15°C.

<sup>1</sup> Red phosphorus exists in several states which require further investigation



The heat evolved by the addition of a large quantity of water to a more or less concentrated solution of some of these gases has been studied. *Berthelot* has found that the *heat of dilution* of hydrochloric acid of the composition  $\text{HCl} + n\text{H}_2\text{O}$  is expressed by the formula  $\frac{11.62}{n}$  Cal.

It is, therefore, inversely proportional to the amount of water primarily united to the acid.

Numbers found ( <i>Berthelot</i> )	Heat of Dilution
$\text{HCl} + 2.17 \text{H}_2\text{O}$ (solution saturated at $-12^\circ\text{C}.$ )	5.31 Cal.
$\text{HCl} + 2.50 \text{H}_2\text{O}$ ( " " " $0^\circ$ )	4.47 "
$\text{HCl} + 3.20 \text{H}_2\text{O}$ . . . . .	3.77 "
$\text{HCl} + 110 \text{H}_2\text{O}$ . . . . .	0.05 "

A quantity of water amounting to about 200 molecules per molecule of  $\text{HCl}$  was used in determining this heat.

For ammonia, dilution of a solution  $\text{NH}_3 + n\text{H}_2\text{O}$  evolves  $\frac{1.27}{n}$  Cal.

By applying the principle of the initial and final states, we can calculate what quantity of heat is evolved by the combining of each successive molecule of water. Thus, for hydrochloric acid:

$\text{HCl}$ evolves on solution . . . . .	17.43 Cal.
$\text{HCl} + 3.2\text{H}_2\text{O}$ evolves on dilution . . . . .	3.77 "

The final states being the same, the difference (13.66 Cal.) corresponds to the difference of the initial states. The solution of  $\text{HCl}$  in the first 3.2 molecules of water therefore evolves 13.66 Cal.

Certain LIQUIDS dissolve in water with evolution of much heat. For *nitric acid*, *Berthelot* has found:

$\text{HNO}_3$	.	.	.	.	Heat of solution	7.15 Cal.
$\text{HNO}_3$	+	$\text{H}_2\text{O}$	.	.	Heat of dilution	3.84 "
$\text{HNO}_3$	+	$2\text{H}_2\text{O}$	.	.	" "	2.32 "
$\text{HNO}_3$	+	$3\text{H}_2\text{O}$	.	.	" "	1.42 "
$\text{HNO}_3$	+	$4\text{H}_2\text{O}$	.	.	" "	0.79 "
$\text{HNO}_3$	+	$5\text{H}_2\text{O}$	.	.	" "	0.42 "
$\text{HNO}_3$	+	$6\text{H}_2\text{O}$	.	.	" "	0.20 "
$\text{HNO}_3$	+	$8\text{H}_2\text{O}$	.	.	" "	-0.04 "
$\text{HNO}_3$	+	$100\text{H}_2\text{O}$	.	.	" "	-0.03 "

For *sulphuric acid*, *Thomsen* has established that at  $18^\circ$  the addition of  $n\text{H}_2\text{O}$  to the acid  $\text{H}_2\text{SO}_4$  evolves

$$\frac{n}{n + 1.86} \times 18 \text{ Cal.}$$

. The methods (direct and indirect) are the same for SOLIDS as for liquids.

According to *Berthelot*, caustic potash (KOH) and its solid di-hydrated derivative ( $\text{KOH} \cdot 2\text{H}_2\text{O}$ ) give out on dissolving 12.46 and  $-0.03$  Cal. respectively. The heat of combination of the  $2\text{H}_2\text{O}$  is consequently 12.49 Cal.

The dilution of concentrated caustic potash solutions, however, gives rise to a considerable thermal effect:

$\text{KOH} + 3\text{H}_2\text{O}$	evolves on dilution	2.55 Cal.
$\text{KOH} + 4\text{H}_2\text{O}$	" "	1.44 "
$\text{KOH} + 10\text{H}_2\text{O}$	" "	0.23 "
$\text{KOH} + 15\text{H}_2\text{O}$	" "	-0.03 "

In presence of  $15\text{H}_2\text{O}$  the hydration of caustic potash has progressed as far as possible.

Let us pass now to the study of SALTS.

Firstly, it may be stated that all salts, *with very rare exceptions*, which do not take up water of crystallisation absorb heat on dissolving. In fact, the solution is accompanied by a breaking down of the molecular grouping of the solid. The solid must suffer a quasi-liquefaction in order that its molecules may become distributed amongst those of the solvent.<sup>1</sup>

<sup>1</sup> We shall see later that the solution of salt molecules is probably attended by a dissociation phenomenon (whereby the acid and the base are set at liberty).

The following are some heats of solution :

$(\text{KCl}, n \text{ aq}) = -4.5 \text{ Cal.}^1$	$(\text{KNO}_3, n \text{ aq}) = - 8.3 \text{ Cal.}$
$(\text{NaCl}, n \text{ aq}) = -1.3 \text{ ,,}$	$(\text{NaNO}_3, n \text{ aq}) = - 4.7 \text{ ,,}$
$(\text{NH}_4\text{Cl}, n \text{ aq}) = -3.9 \text{ ,,}$	$(\text{NH}_4\text{NO}_3, n \text{ aq}) = - 6.2 \text{ ,,}$
$(\text{KI}, n \text{ aq}) = -5.2 \text{ ,,}$	$(\text{KClO}_3, n \text{ aq}) = -10.0 \text{ ,,}$
$(\text{KCN}, n \text{ aq}) = -2.9 \text{ ,,}$	$(\text{K}_2\text{SO}_4, n \text{ aq}) = - 6.6 \text{ ,,}$
$(\text{LiCl}, n \text{ aq}) = +8.4 \text{ ,,}$	$(\text{K}_2\text{CrO}_4, n \text{ aq}) = - 5.3 \text{ ,,}$
$(\text{LiNO}_3, n \text{ aq}) = +0.3 \text{ ,,}$	

A certain number of salts crystallise with molecules of water. It is necessary to admit that they have a particular avidity for the solvent, and on solidifying they retain a certain proportion of it. The heat of solution of these salts taken in the anhydrous condition is generally positive and in all cases higher than that of the hydrated compound.

Examples :

$(\text{NaI}, n \text{ aq}) = 1.3 \text{ Cal.}$	$(\text{FeCl}_2, n \text{ aq}) = 18.0 \text{ Cal.}$
$(\text{NaI } 2\text{aq}, n \text{ aq}) = - 4.0 \text{ ,,}$	$(\text{FeCl}_2 \text{ } 2\text{aq}, n \text{ aq}) = 3.3 \text{ ,,}$
$(\text{CaCl}_2, n \text{ aq}) = 17.4 \text{ ,,}$	$(\text{CoCl}_2, n \text{ aq}) = 18.4 \text{ ,,}$
$(\text{CaCl}_2 \text{ } 6\text{aq}, n \text{ aq}) = - 4.4 \text{ ,,}$	$(\text{CoCl}_2 \text{ } 6\text{aq}, n \text{ aq}) = - 2.8 \text{ ,,}$
$(\text{Ca}(\text{NO}_3)_2, n \text{ aq}) = 4.0 \text{ ,,}$	$(\text{Na}_2\text{SO}_4, n \text{ aq}) = 0.44 \text{ ,,}^*$
$(\text{Ca}(\text{NO}_3)_2 \text{ } 4\text{aq}, n \text{ aq}) = - 7.6 \text{ ,,}$	$(\text{Na}_2\text{SO}_4 \text{ } 10\text{aq}, n \text{ aq}) = -18.2 \text{ ,,}$

The difference between the heats of solution of the anhydrous and the hydrated salts is termed the *heat of hydration* (application of the principle of the initial and final states).

### Neutralisation Phenomena

The heat of neutralisation of a base by an acid is generally determined *in dilute aqueous solution*. The calorimetric operation can then be easily carried out, and, since the conditions of the experiment are almost the same for all salts, *the thermal effects found are comparable amongst themselves*.

<sup>1</sup> The equations are written according to Thomsen's method.

*n aq* = much water, 100 to 200 molecules.

The table given, taken from *Berthelot's 'Essai de mécanique chimique,'* shows the heat of neutralisation of a number of bases and acids. The heats are expressed in large calories.

BASES	CHLORIDES HCl (1 eq.) in 2 litres	NITRATES HNO <sub>3</sub> in 2 litres	ACETATES C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> in 2 litres	FORMATES CH <sub>3</sub> O <sub>2</sub> in 2 litres	OXALATES 1/3 C <sub>2</sub> H <sub>2</sub> O <sub>4</sub> in 4 litres	SULPHATES 1/2 H <sub>2</sub> SO <sub>4</sub> in 2 litres	SULPHIDES 1/2 H <sub>2</sub> S in 8 litres	CYANIDES HCN in 2 litres	CARBONATES 1/2 CO <sub>2</sub> in 15 litres
NaOH	13·7	13·7	13·3	13·4	14·3	15·85	3·85	2·9	10·2
KOH	13·7	13·8	13·3	13·4	14·3	15·7	3·85	3·0	10·1
NH <sub>3</sub>	12·45	12·5	12·0	11·9	12·7	14·5	3·1	1·3	5·3
1/2 CaO <sup>1</sup>	14·0	13·9	13·4	13·5	18·5	15·6	3·9	3·2	9·8
1/2 BaO <sup>1</sup>	13·85	13·9	13·4	13·5	16·7	18·4		3·2	11·1
1/2 SrO <sup>1</sup>	14·0	13·9	13·3	13·5	17·6	15·4		3·1	10·5
1/2 MgO	13·8	13·8				15·6			9·0
1/2 MnO	11·8	11·7	11·3	10·7	14·3	13·5	5·1		6·8
1/2 FeO	10·7		9·9			12·5	7·3		5·0
1/2 NiO	11·3					13·1			
1/2 CoO	10·6					13·3			
1/2 CdO	10·1	10·1				11·9		7·2	
1/2 ZnO	9·8	9·8	8·9	9·1	12·5	11·7	9·6	7·3	5·5
1/2 PbO	7·7	7·7	6·5	6·6	12·8	10·7	13·3		6·7
1/2 CuO	10·7	(cryst. allise d)		6·6		9·2	15·8		2·4
1/2 HgO	7·5	7·5	6·2		7·0		24·3	15·5	
1/2 Ag <sub>2</sub> O	9·45		3·0				27·9	20·9	6·9
1/2 Al <sub>2</sub> O <sub>3</sub>	20·1	5·2	4·7		12·9	7·2			
1/2 Fe <sub>2</sub> O <sub>3</sub>	9·3					10·5			
1/2 Cr <sub>2</sub> O <sub>3</sub>	5·9	5·9	4·5			5·7			
	6·9					8·2			

<sup>1</sup> The hydrates dissolved in 25, 6, and 10 litres of water respectively. The following oxides are taken as more or less hydrated precipitates.

*Conditions of the Calorimetric Experiment.*—Alkaline bases are dissolved in two litres of water for each equivalent of base; for the bases of the alkaline earths a much larger proportion of water is taken. One equivalent of acid is dissolved in the quantity of water denoted in the table for acting on the soluble bases, and in at least four

litres of water for acting on the insoluble metallic hydrates.<sup>1</sup>

We see that certain acids in combining with the same base evolve almost the same quantities of heat, and in the same way certain bases are *isodynamic* towards the same acid. Thus the strong monobasic acids, such as HCl, HBr, HI, HNO<sub>3</sub>, HClO<sub>3</sub>, HBrO<sub>3</sub>, HIO<sub>3</sub>, HClO<sub>4</sub>, and the organic sulphonic acids, on neutralisation with caustic soda evolve quantities of heat which vary only within narrow limits (from 13·4 to 14 Cal.). To this list the acids of the acetic acid series may be added, as far as their action on a strong base is concerned. The weak acids, such as HClO, HCN, &c., have a relatively low heat of neutralisation (9·8 and 2·9 Cal.).

The alkaline and alkaline-earth bases, and, we may also add, the tetra-substituted ammonium- and tri-substituted sulphonium-hydroxides, form an *isodynamic* group wherein the heat of neutralisation by hydrochloric acid varies from 13·6 to 14 Cal. With ammonia the evolution of heat is much smaller. And the thermal effect of the neutralisation of the oxides of the heavy metals and of the sesquioxides of the aluminium group is still smaller (in this connection we may recall the feeble stability of the salts formed from these sesquioxides).

Concerning the action of a weak acid on a weak base

<sup>1</sup> An equivalent of hydrochloric acid is equal to one gram-molecule.

That quantity of a base or of an acid which is capable of saturating or replacing one gram-molecule of hydrochloric acid is its *equivalent*.

The following are equivalents :

1	gram-molecule of hydrochloric
1	“ “ caustic soda
$\frac{1}{2}$	“ “ lime
$\frac{1}{2}$	“ “ sulphuric acid

and so on.

We even speak of an equivalent of a salt : NaCl, AgNO<sub>3</sub>,  $\frac{1}{2}$ Na<sub>2</sub>SO<sub>4</sub>,  $\frac{1}{3}$ Na<sub>3</sub>PO<sub>4</sub>, &c.

it is to be noticed that the thermal effect may be influenced by the degree of dilution of the reacting solutions, and that in certain cases (notably for carbonic acid and ammonia) the solution of the neutral salt may give an evolution of heat on the addition either of excess of acid or excess of base.

If we examine the table a little more closely, we see that there is an almost constant difference between the corresponding numbers of two vertical columns, and the same applies to two horizontal series. In other words, the difference between the heats of neutralisation of the acids  $a, b, c, \dots$  by the same base remains almost constant whatever be the base employed. We find the same thing for the heats of neutralisation of several different bases  $a', b', c', \dots$  by the same acid.

We conclude from this that *the heat of neutralisation is composed additively of two factors, one of which depends entirely on the nature of the base and the other only on the nature of the acid.*<sup>1</sup> These factors preserve a fixed and invariable value, and it seems, therefore, that it would be quite incorrect to try to deduce from the heats of neutralisation a measure of the affinities which operate between acids and bases.<sup>2</sup>

Hess's LAW OF THERMONEUTRALITY gives us the most general expression for this state of things. This law states that no thermal effect is produced by mixing two dilute salt solutions, whatever be the state of equilibrium resulting from the reaction. The law is in agreement with observed facts, provided that we are dealing only with salts

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<sup>1</sup> A similar rule applies to the changes of volume which accompany neutralisation phenomena. This will be pointed out and demonstrated later (in the fourth part).

<sup>2</sup> Let us compare this with the law of gravitation. The attraction which is exercised between two bodies is proportional to the *product* of their masses. The heat of neutralisation, which corresponds to the formation of a salt, is composed, on the contrary, of the *sum* of two factors, and therefore does not appear to express the mutual attraction between the base and the acid.

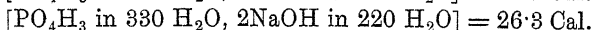
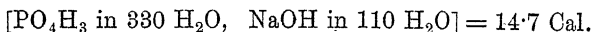
constituted by the union of strong acids and strong bases, and that the mixture does not give rise to the formation of any precipitate. Every condensation of matter gives rise to an abnormal thermal effect.

It would be difficult at this part of the course to give an interpretation of these phenomena, and this is reserved for later chapters. Towards the end of the third part, we shall see to what process the heats of neutralisation must be attributed; and still further on we shall have occasion to study more closely the nature of the relationships which are established between the base and the acid in a salt solution.

The study of heats of neutralisation may now be closed by some remarks on the polybasic acids.

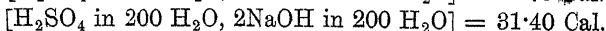
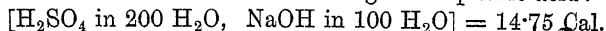
The different basicities of *some* of these acids lead to the same thermal effect. As an example of this class tri-carballylic acid  $[C_3H_5(COOH)_3]$  may be quoted. The progressive saturation of this acid by one, two, and three equivalents of caustic potash evolves 13.2, 26.8 (or  $13.4 \times 2$ ) and 39.75 (or  $13.25 \times 3$ ) Calories.

Other polybasic acids behave in quite a different manner, and, as examples, phosphoric acid and arsenic acid may be specially mentioned.



The evolution of heat is therefore 14.7 Cal. for the first NaOH, 11.6 Cal. for the second, and 7.3 Cal. for the third. It may be added that an excess of the base produces a further evolution of heat (1.2 Cal. for the fourth molecule and 0.3 Cal. for the fifth).

*Thomsen* has found the following for sulphuric acid :



*i.e.* 14.75 Cal. for the first molecule and 16.65 Cal. for the

second. In this case the addition of an excess of soda does not give rise to a supplementary evolution of heat.

On the contrary the addition of dilute acid to a dilute solution of the neutral sulphate causes an absorption of heat, which *Thomsen* expresses by the equation :

$$\frac{1}{2}[\text{Na}_2\text{SO}_4 \text{ aq}, n\text{H}_2\text{SO}_4 \text{ aq}] = - \frac{n}{n + 0.8} 1.65 \text{ Cal.}$$

Therefore when  $n = 1$ ,

$$\frac{1}{2}[\text{Na}_2\text{SO}_4 \text{ aq}, \text{H}_2\text{SO}_4 \text{ aq}] = - 0.92 \text{ Cal.}$$

We here meet with an endothermic reaction to which we shall refer later.

### *Organic Substances*

The application of thermo-chemistry to the study of organic compounds constitutes a problem the solution of which obtrudes as much on the industrial as on the physiological point of view. In the industries fuel is burned to give motion to the machinery, and animal life has its only source of energy in the oxidation phenomena which take place in the various tissues. Unfortunately, organic compounds, as a rule, cannot be synthesised by rapid and complete reactions which lend themselves to calorimetric examination. We know only one method of investigation—an indirect method based on the principle of the initial and final states.

A complete combustion of the organic material is carried out in the calorimeter, and the heat evolved corresponds to a *final state*, represented by a certain number of molecules of liquid water and of gaseous carbon dioxide. (In some cases nitrogen, nitric acid, sulphurous acid, sulphuric acid [more or less hydrated], phosphoric acid, &c., may be formed.) Now we can attain the *same final state* by burning the requisite quantity of carbon (diamond) and of free hydrogen (taking into account also the requisite amount, if any, of nitrogen, sulphur, phosphorus, &c.). But different heats will be evolved in these two operations.



The difference found evidently corresponds to the difference which existed *between the initial states*, and expresses the heat of formation of the organic substance from its elements.

In a word, the heat of combustion of an organic substance is lower than that of the elements which it contains by that quantity of heat which is evolved when the elements unite to form the compound.

For a compound  $C_xH_yO_z$ , the heat of formation is therefore equal to

$$x(C, O_2) + \frac{y}{2}(H_2, O) - f(C_xH_yO_z).$$

For carbon, taken as diamond,  $(C, O_2) = 94.31$  Cal. For liquid water  $(H_2, O) = 69$  Cal. If we wish to know the heat of formation from amorphous carbon, then we must take  $(C, O_2) = 97.65$  Cal. (Berthelot's figures).

The third term,  $f(C_xH_yO_z)$  expresses the value found experimentally for the heat of combustion of the organic substance.

The heat of combustion has been determined for a large number of substances. But the numbers found had rather a doubtful value, and might, particularly for compounds containing sulphur, chlorine, &c., be infected with a considerable error. Since the introduction of *Berthelot's* CALORIMETRIC BOMB, however, it has been possible to determine the heat of combustion of organic substances more accurately.

The form of this apparatus is shown in fig. 37.

The apparatus consists of a very strong vessel and cover of steel, nickelled on the outside and lined in the interior with some non-oxidisable material, such as platinum, gold, or enamel (*Mahler*). The cover is fitted on to the vessel by means of a piece of steel screwed to the body of the bomb. The cover has several appendages. The central tubulus A is made of steel, and contains a screw which serves as a valve and as the inlet pipe for the

oxygen. The other appendages are thick platinum wires; one of them (B) is in metallic connection with the body of the bomb and serves as a support for the substance to be burnt; the other (C) is insulated by ivory or caoutchouc joints and can be connected with a pole of a battery.

If the substance to be burnt is solid, it is used in the form of a small compressed cylinder. If it is liquid, it is contained in a small platinum capsule; and if it is easily volatile, the containing vessel may be provided with a cover of collodion. The material is placed on the platinum support, and above it the two thick wires are connected by a thin spiral of iron wire. The bomb is closed and oxygen introduced through A, until there is a pressure inside of 25 atmospheres. The screw valve is then tightened and the bomb immersed in the water of a calorimeter (provided with a mechanical stirrer).

After a preliminary period, which lasts only a few minutes, the principal period is introduced by starting the combustion of the iron spiral and the organic substance by means of an electric current. The regular descent of the thermometer, that is the final period, generally commences after four or five minutes. The whole operation lasts only about a quarter of an hour, during which the temperature is read off at the commencement of each minute. The

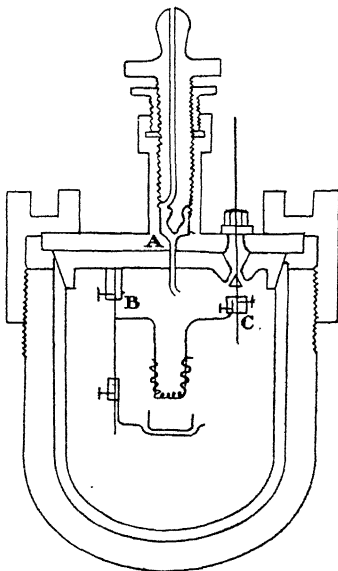


FIG. 37

numbers necessary for the calculation of the true maximum temperature are thus obtained (see page 143).

To calculate the heat evolved the water equivalents of all the instruments must be known. For the bomb itself this is very considerable. It may be calculated from a very exact knowledge of the weight and specific heat of the various parts of the instrument. The water equivalent of the bomb may also be ascertained by burning in it a known weight of a substance whose heat of combustion is very exactly known (naphthalene, camphor, &c.). The quantity of heat evolved is known, and the calorimetric calculation contains only a single unknown—the water-equivalent of the bomb. We may also arrive at this value simply by the method of mixture. The bomb (at a known temperature) is immersed in a known weight of water (at a somewhat higher temperature, *e.g.* 60°), and from the final temperature of the system we may easily calculate the calorific capacity of the bomb.

The quantity of material used must be such that at least two-thirds of the oxygen remains in excess, and it is necessary to take into account the water-equivalent of the oxygen compressed in the apparatus. Further, as commercial oxygen (compressed in cylinders to 100 atmospheres pressure) may contain up to 10 per cent. of nitrogen, a certain quantity of nitric acid is formed by the combustion. This quantity of acid must be determined and its heat of formation deducted from the general result. The heat of combustion of the small iron spiral has also to be deducted. In order to make it unnecessary to take into account the evaporation of a part of the water produced, oxygen saturated with water vapour is used. It suffices for this to introduce into the bomb a known weight of water (which, of course, increases the water equivalent of the apparatus).

For data concerning the employment of an auxiliary combustible (for certain substances which do not burn easily), or the combustion of substances containing sulphur,

chlorine, &c., *Berthelot's* 'Calorimétrie pratique' may be consulted with advantage.

In order to make the harmony of the operation and the calculation clearer, I cite an example (taken from the work referred to) :

*Combustion of carbon* (charcoal purified by chlorine at a red heat).

0.437 gm. charcoal; ash, 0.0028 gm.;  
real carbon, 0.4342 gm.

*Preliminary period*; temperatures read :

After 0 minute	17.360°	After the 3rd minute	17.360°
After the 1st "	17.360°	" 4th "	17.360°
" 2nd "	17.360°		

*Combustion* :

After the 5th minute	18.500°	After the 7th minute	18.820°
" 6th "	18.782°	" 8th "	18.818°

*Final period* :

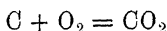
After the 9th minute	18.810°	After the 12th minute	18.785°
" 10th "	18.802°	" 13th "	18.775°
" 11th "	18.795°	" 14th "	18.770°
Initial cooling per minute	0.00		
Final " "	+ 0.008		
Correction for the temperature $\Sigma \Delta$	= 0.026		

*Rise in temperature* :

Uncorrected :  $18.818^\circ - 17.360^\circ = 1.458^\circ$   
Corrected : .....  $1.484^\circ$

Water-equivalent of the calorimeter, bomb, compressed oxygen, thermometer, &c. . . . .	2,398.4 gm.
Weight of nitric acid formed . . . . .	0.0173 gm.
Total heat observed . . . . .	3,559.2 cal. :
of which for the combustion of the iron spiral . . . . .	22.4
for the formation of dilute nitric acid . . . . .	3.9
for the combustion of the carbon . . . . .	3,532.9 cal.
1 gram of carbon evolves . . . . .	8,136.6 "
12 grams (one gram atomic weight) evolves . . . . .	97.64 Cal.

The number thus obtained can be used directly because the reaction



is not accompanied by any change of volume and produces the same thermal effect under constant volume or under constant pressure.

But it must be borne in mind that in the calorimetric bomb we work *at constant volume*, and it is generally necessary to introduce a correction in order to arrive at the number which would be obtained if the combustion had been carried out *under constant pressure*. If we denote by  $Q_{iv}$  the heat evolved in the bomb by one gram-molecule of substance, by  $N$  the number of molecular volumes occupied by the gaseous matter before the combustion, and by  $N'$  the number of molecular volumes occupied by the gaseous products of the reaction, then the heat which would be evolved under constant pressure can be found from the equation,

$$Q_{ip} = Q_{iv} + (N - N') (0.54 + 0.002t).$$

$t$  denotes the mean temperature of the calorimetric measurements.<sup>1</sup>

The combustion of naphthalene takes place according to the equation  $\text{C}_{10}\text{H}_8 + 12\text{O}_2 = 10\text{CO}_2 + 4\text{H}_2\text{O}$ ; it is accompanied by a condensation of two molecular volumes and at  $15^\circ$  requires as correction an addition of 1.14 Cal.

The correction may be negative, as is the case with formic acid;  $\text{CH}_2\text{O}_2 + \text{O} = \text{CO}_2 + \text{H}_2\text{O}$ .

Here  $(N - N') = -\frac{1}{2}$ , and at  $15^\circ$  it is necessary to subtract 0.28 Cal.

<sup>1</sup> The volume occupied by solids or liquids is negligible, and does not enter into the calculation. To understand the equation the reader should refer to the explanations on page 153.

In this résumé of thermo-chemistry we do not desire to give too many numerical data. The following tables give the thermo-chemical numbers for a few of the most important series of substances.

The heats of *combustion* and *formation* are given for the temperature 15°, under constant pressure and starting from carbon in the form of diamond.

## HYDROCARBONS

Name	Formula	Heat of Formation		Heat of Combustion
		Gas	Liquid	
Methane . . .	CH <sub>4</sub>	18.8		213.5 Cal.
Ethane . . .	C <sub>2</sub> H <sub>6</sub>	23.3		372.3 "
Propane . . .	C <sub>3</sub> H <sub>8</sub>	30.5		528.4 "
Butane, normal . .	C <sub>4</sub> H <sub>10</sub>	35.0		687.2 "
Hexane, normal . .	C <sub>6</sub> H <sub>14</sub>		57.6	991.2 "
Di-isopropane . .	C <sub>6</sub> H <sub>14</sub>	49.9		998.9 "
Ethylene . . .	C <sub>2</sub> H <sub>4</sub>	-14.6		341.1 "
Propylene . . .	C <sub>3</sub> H <sub>6</sub>	-9.4		499.3 "
Isobutylene . . .	C <sub>4</sub> H <sub>8</sub>	2.6		650.2 "
Amylene (ordinary) .	C <sub>6</sub> H <sub>10</sub>	7.3		811.3 "
Acetylene . . .	C <sub>2</sub> H <sub>2</sub>	-58.1		315.7 "

As the sum of the heats of combustion of 2C and 3H<sub>2</sub> is, according to *Berthelot*, equal to  $(94.3 \times 2) + (69 \times 3) = 395.6$  Cal., and the combustion of *ethane* liberates 372.3 Cal., therefore the difference 23.3 Cal. represents the heat of formation of this hydrocarbon.

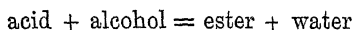
We may notice that in the case of the saturated hydrocarbons a difference of CH<sub>2</sub> in the molecular constitution corresponds to an almost constant difference of 158 Cal. in the heat of combustion. A similar regularity is noticed in the case of other homologous series.

## ALCOHOLS AND ACIDS OF THE FATTY SERIES

Name	Formula	Heat of Formation				Heat of Combustion
		Gas	Liquid	Solid	Dissolved	
Methyl alcohol	$\text{CH}_3\text{OH}$	53.3	61.7*		63.7	Cal. 170.6
Ethyl "	$\text{C}_2\text{H}_5\text{OH}$	59.8	69.9*		72.4	325.7
Propyl "	$\text{C}_3\text{H}_7\text{OH}$	68.6	78.6*		81.7	480.3
Isopropyl "	$\text{C}_3\text{H}_7\text{OH}$		80.6*		84.4	478.3
Isobutyl "	$\text{C}_4\text{H}_9\text{OH}$		85.5*		88.4	636.7
Amyl "						
(ordinary) "	$\text{C}_5\text{H}_{11}\text{OH}$	80.9	91.6*		94.4	793.9
Capryl alcohol	$\text{C}_8\text{H}_{17}\text{OH}$		113.3*			1,262.1
Glycerine	$\text{C}_3\text{H}_8\text{O}_3$		161.7*	165.6	167.1	397.2
Formic acid	$\text{CH}_2\text{O}_2$	96.7	101.6*	104.0	101.6	61.7
		at 100°				
		112.2				
Acetic "	$\text{C}_2\text{H}_4\text{O}_2$	120°	117.2*	119.7	117.6	209.4
		112.5				
Propionic "	$\text{C}_3\text{H}_6\text{O}_2$		122.5*		123.1	367.4
Butyric "	$\text{C}_4\text{H}_8\text{O}_2$		128.8*	130.3	129.4	524.4
Isobutyric "	$\text{C}_4\text{H}_8\text{O}_2$		135.2*		136.2	518.0
Palmitic "	$\text{C}_{16}\text{H}_{32}\text{O}_2$			241.0*		2,371.8?
				214.0		2,398.4?
Stearic "	$\text{C}_{18}\text{H}_{36}\text{O}_2$			227.6*		2,677.8?
				261.6		2,711.8?

N.B.—The heats of formation marked with an asterisk (\*) are those which have been directly derived from the heats of combustion.

ORGANIC ACID ESTERS.—Their heat of combustion is generally a little higher than the sum of the heats of combustion of the alcohol and of the acid. The reaction



is slightly endothermic. It is also generally slow and incomplete.

The following tables are important from a physiological point of view.

## CARBOHYDRATES

Name	Formula	Heat of Formation in the solid state	Heat of Combustion
Dextrose . . .	$C_6H_{12}O_6$	302.6	677.2 Cal.
Fructose (levulose) .	id.	303.9	675.9 "
Galactose . . .	id.	309.9	669.9 "
Saccharose . . .	$C_{12}H_{22}O_{11}$	535.6	1,355.0 "
Lactose . . .	id.	537.4	1,351.4 "
Maltose . . .	id.	538.1	1,350.7 "
Dextrin . . .	$(C_6H_{10}O_5)_n$	n. 243.6	n. 667.2 "
Starch . . .	id.	n. 225.9	n. 684.9 "
Cellulose . . .	id.	n. 230.4	n. 680.4 "
Glycogen . . .	id.	n. 228.9	n. 678.9 "

The mean value for the heat of combustion of a quantity of the substances containing 1 gram of carbon may be taken as 9.4 Cal.

NATURAL FATS.—It has been found that the combustion of one gram of animal fat or vegetable oil evolves on the average 9.5 Calories; in the case of butter, 9.23 Cal.

The combustion of a quantity of fat containing one gram of carbon evolves 12.4 Cal.

## ALBUMINOIDS

	Heat of Combustion		Heat of Formation	
	Of one gram of substance	Of a quantity containing one gram of carbon	Of one gram of substance	Of a quantity containing one gram of carbon
Egg albumen . . .	5.69	10.99	0.874	1.689 Cal.
Fibrin . . .	5.53	10.82	0.918	1.796 "
Fat-extracted flesh .	5.73	10.67	1.137	2.117 "
Hæmoglobin . . .	5.91	10.68	1.066	1.931 "
Casein . . .	5.63	11.08	0.927	1.825 "
Egg-yolk (with 7 per cent. of nitrogen) .	8.124	12.05	0.828	1.228 "
Gluten . . .	5.995	10.88	0.999	1.795 "
Peptone . . .	5.299	10.576		
Average . . .	5.691	10.870		



These numbers were determined by *Berthelot and André*. They agree sufficiently well with those determined by *Stohmann*.

In the animal economy the combustion of albuminoids does not produce free nitrogen, but stops at the formation of more or less complex amido-compounds. *In man 80 to 85 per cent. of the nitrogen is transformed into urea*. If the nitrogen were wholly transformed to this, the heat of combustion of a quantity of the albuminoid substance containing one gram of carbon would be reduced to 9.13 Cal.

Certain other elimination-forms of the nitrogen give rise to a still greater loss of heat, as the following table shows :

Name	Formula	Total Combustion of one gram-molecule	Organic Combustion (all the substances dissolved and the nitrogen eliminated as urea). Numbers from <i>Berthelot and Petit</i> or <i>Berthelot and André</i>
Urea . . .	$\text{CH}_2\text{N}_2\text{O}$	151.5 Cal.	—
Uric acid . . .	$\text{C}_5\text{H}_4\text{N}_4\text{O}_3$	461.4 "	175.8 Cal.
Hippuric acid . .	$\text{C}_9\text{H}_8\text{NO}_3$	1,012.9 "	932.8 "
Glycoccol . . .	$\text{C}_6\text{H}_5\text{NO}_2$	234.9 "	167.3 "
Alanine . . .	$\text{C}_3\text{H}_7\text{NO}_2$	389.2 "	327.5 "
Leucin . . .	$\text{C}_6\text{H}_{13}\text{NO}_2$	855.9 "	811.2 "
Tyrosin . . .	$\text{C}_9\text{H}_{11}\text{NO}_3$	1,071.2 "	942.6 "

A general remark applicable to all these compounds (except urea and leucin) is that the observed heat of combustion is greater than the value calculated according to the hypothesis of *Dulong* (or of *Welter*). These scientists believed that the heat of combustion of an organic body can be obtained by eliminating in the form of water as much hydrogen as possible, then adding together the heats of combustion of the residual hydrogen and of the carbon, both considered in the free state. According to this theory, the heat of combustion of a carbohydrate would be equal to that of the carbon contained in it (in reality, it is greater).

## AROMATIC SUBSTANCES

Name	Formula	Heat of Formation				Heat of Combustion
		Gas	Liquid	Solid	Dissolved	
Benzene . . .	$C_6H_6$	-11.3*	-4.1*	-1.8		Cal. 784.1 776.9
Naphthalene . .	$C_{10}H_8$	-27.4	-22.8*			1,241.8
Phenol . . .	$C_6H_5O$		34.5	36.8*	34.2	736.0
Resorcin . . .	$C_6H_4O_2$			89.4*	85.8	683.4
Hydroquinone . .	id.			87.3*	82.9	685.5
Pyrocatechin . .	id.			87.6*	84.1	685.2
Cresol, ortho- . .	$C_7H_8O$			56.3*	54.2	879.8
• „ para- . . .	id.			55.1*		881.0
• „ meta- . . .	id.			55.7*	53.6	880.4
Benzoic acid . .	$C_7H_6O_2$		91.9	94.2*	87.8	772.9
Benzaldehyde . .	$C_7H_6O$		25.4*			841.7
Benzyl alcohol . .	$C_8H_8O$			40.8*		895.3
Methyl benzoate .	$C_8H_8O_2$		86.8*			944.0
Salicylic acid . .	$C_7H_6O_3$			132.1*	125.7	735.0
Paraoxybenzoic acid . . .	id.			141.2*	135.0	725.9
Metaoxybenzoic acid . . .	id.			138.1*	132.5	729.0
Aniline . . .	$C_6H_5N$	-11.2*				818.5
Azobenzene . . .	$C_{12}H_{10}N_2$	-79.2*				1,555.8
Nitrobenzene . .	$C_6H_5NO_2$		5.1*	7.8		733.2
Meta-dinitrobenzene . .	$C_6H_4N_2O_4$			6.8*		697.0
Phenylhydrazine .	$C_8H_8N_2$		36 *	38.6	36.5	805.8
Terebenthene . .	$C_{10}H_{16}$	-5.2	4.2*			1,490.8
Camphor . . .	$C_{10}H_{16}O$			80.3*		1,414.7

The asterisk (\*) denotes the heat of formation directly calculated from the heat of combustion.

For the higher homologues of the aromatic substances the heats of combustion can be obtained sufficiently closely by adding 155 Cal. for each additional  $CH_2$  group. As for the fatty compounds, so in general with the aromatic substances, the heat of combustion is only strongly influenced by isomerism in so far as it affects the linkages which exist between the carbon atoms (single, double, or triple bonds).

## JULIUS THOMSEN'S SYSTEM

This author believes that we can deduce the quantity of heat necessary for the volatilisation and isolation of an atom of carbon (volatilisation and isolation of the atoms contained in 12 grams of carbon). His system is based on the data :

$$\left. \begin{array}{l} (C, O) = 29.29 \text{ Cal.} \\ (C, O_2) = 96.96 \text{ ,,} \end{array} \right\} \begin{array}{l} \text{for amorphous carbon and under} \\ \text{constant volume,}^1 \end{array}$$

and on the hypothesis, *a priori* quite admissible, that the four atomicities of carbon are identical and, consequently, that by the fixation of the first and of the second oxygen atom the same quantity of heat is evolved. At first sight this is not apparent, on the contrary the thermal effects are very different (29.29 and 67.67 Cal.); but this is due to the fact that the fixation of the first oxygen atom must furnish the heat necessary for the isolation of the carbon atoms. This isolation absorbs  $67.67 - 29.29 = 38.38$  Cal.

Thomsen then proceeds to determine the thermal effect developed by the different relationships which are established between the atoms in organic molecules. For the hydrocarbons (all the products being supposed gaseous and at the temperature  $18^\circ$ ) he finds :

	Under constant pressure		Under constant volume
	Heat of combustion	Heat of formation	Heat of formation
$CH_4$ . . .	211.93 Cal.	21.75 Cal.	21.17 Cal.
$C_2H_2$ . . .	310.05 "	-47.77 "	-47.77 "
$C_2H_4$ . . .	333.35 "	-2.71 "	-3.29 "
$C_2H_6$ . . .	370.44 "	28.56 "	27.40 "

<sup>1</sup> To discuss *J. Thomsen's* system we must admit his fundamental data for the meantime :

$$\begin{array}{l} (H_2, O) = 68.36 \text{ Cal. (liquid water)} \\ (C, O_2) = 96.96 \text{ ,, (for amorphous carbon)} \\ (C, O) = 29.0 \text{ ,, under constant pressure} \\ (C, O) = 29.29 \text{ ,, under constant volume.} \end{array}$$

This last figure is larger than the second last on account of an external work equal to  $\frac{1}{2}(0.58)$  Calories being avoided under the conditions of the experiment. See page 153.

The numbers in the last column are derived from those in the second column by subtraction of 0.58 Cal. for each molecular volume which has disappeared in the formation of the organic substance. For methane, the reaction  $C + 2H_2 = CH_4$  gives rise to a condensation of one molecular volume. The heat of *formation* under constant volume is therefore  $21.75 - 0.58 = 21.17$  Cal.

Passing now to the analysis of the thermal effects accompanying the formation of the hydrocarbons and denoting by:

$d$ , the quantity of heat necessary to bring about the disintegration of one gram-atom of carbon;

$v_1$ , the heat evolved when two atoms of carbon unite with a single bond;

$v_2$ , the same with a double bond;

$v_3$ , the same with a triple bond;

$q$ , the quantity of heat evolved when one atom of hydrogen separates from the hydrogen molecule and unites with an atom of carbon; we can express these effects in the following manner:

$$(C, H_4) = -d + 4q = 21.17 \text{ Cal.}$$

$$(C_2, H_2) = -2d + v_3 + 2q = -47.77 \text{ ,,}$$

$$(C_2, H_4) = -2d + v_2 + 4q = -3.29 \text{ ,,}$$

$$(C_2, H_6) = -2d + v_1 + 6q = 27.40 \text{ ,,}$$

The value of  $d$  is known. We have, therefore, a system of four equations containing four unknowns, leading to the solutions:

$$v_3 = 0; v_2 = v_1 = 14.2; q = 15$$

These are the figures by the aid of which *Thomsen* has calculated the heat of *formation* of a certain number of other hydrocarbons, and his theoretical results have been confirmed by experiment.

The calculated heat of formation of benzene according to *Kekulé's* formula is  $-55.08$  Cal., and for any other formula with nine single bonds  $-12.48$  Cal. The

value deduced from the heat of combustion of benzene is equal to  $786.84 - 799.35 = -12.51$  Cal. under constant pressure, which is equivalent to  $-13.67$  Cal. at constant volume. This number is not in agreement with either of those furnished by theory. It corresponds, however, fairly well with a formula with nine single linkages.<sup>1</sup>

The road once opened, it has been possible for *Thomsen* to go much further and to determine the thermal effect corresponding to other interatomic relationships. He has studied, for example, the successive substitution of four atoms of chlorine for the four atoms of hydrogen in methane, and he has found that these four successive operations do not evolve the same quantity of heat. He has further found that the fixation of a hydroxyl group (OH) on to a carbon atom is accompanied by an evolution of heat which varies according as the compound formed is an alcohol or an acid.

The thermal effect of the fixation of an atom or of a radical on to carbon depends, therefore, to a certain degree on the nature of the union of the carbon before this fixation.

The facts and the conclusions which we have just arrived at evidently appear to contradict the starting point of *Thomsen's* system. For *Thomsen's* fundamental hypothesis was that, apart from the heat necessary for the isolation of the carbon atom, the reactions  $[C, O]$  and  $[CO, O]$  should produce the same thermal effect.

### THE LAW OF MAXIMUM WORK

Mechanics teaches us that a system of material points is in equilibrium when the sum of the forces acting on the system has produced the greatest possible quantity of work. A very general rule, which has for a long time been raised to the height of a principle, determines in an

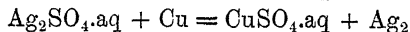
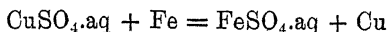
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<sup>1</sup> The heat of combustion of benzene (in the state of vapour at  $18^{\circ}$ ) is, according to *Thomsen*,  $799.35$  Cal.

- analogous manner the effect produced by the forces which act between the atoms. *Every change, accomplished without the intervention of a foreign energy, tends towards the production of that substance or system of substances whereby the greatest heat is evolved (Berthelot, 1879).<sup>1</sup> Every simple or complex action of a purely chemical nature is accompanied by an evolution of heat (Thomsen, 1853).<sup>2</sup>*

In general this is the case, and we may say that this rule is in agreement with observed facts. Thus at low temperatures water is only decomposed by those metals whose heat of oxidation is higher than that of hydrogen. And in the same way the action of metals on dilute acids is determined; the metal dissolves with evolution of hydrogen, only if it can form a salt whose heat of formation is greater than that of the acid employed.

- The replacement of one metal by another in a salt solution likewise may only take place exothermically. The reactions



take place with evolution of heat (35 to 37 Cal.).

Direct substitution reactions generally conform to the law of maximum work. By combination with hydrogen and the metals, chlorine evolves more heat than bromine, and this latter more than iodine. Hydriodic acid and the iodides are decomposed by bromine and by chlorine, but hydrobromic acid and the bromides are only decomposed by chlorine.

On the other hand, iodine is substituted for chlorine

<sup>1</sup> 'Tout changement accompli sans l'intervention d'une énergie étrangère tend vers la production du corps ou du système de corps qui dégage le plus de chaleur.'

<sup>2</sup> 'Jede einfache oder zusammengesetzte Wirkung rein chemischer Natur ist von einer Wärmeentwicklung begleitet.'

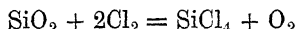
when it reacts on chloric acid, because the heat of formation of this acid is less than that of iodic acid.

We cannot consider as being in opposition to this rule, whose study we are pursuing, certain endothermic transformations, realised by a reaction where the whole produces a positive thermal effect. Examples :

(1.) The transformation of silver iodide into the chloride by direct action of chlorine evolves 14.8 Cal. Yet the reverse transformation according to the reaction  $\text{AgCl} + \text{HI} = \text{AgI} + \text{HCl}$  is possible, because this double decomposition corresponds to an evolution of

$$-(29.0 - 6.4) + (14.2 + 22) = 13.6 \text{ Cal.}$$

(2.) The preparation of silicon tetrachloride by the action of chlorine on silica is impossible, because the reaction



would correspond to a thermal effect of  $-179.6 + 121.8 = -57.8$  Cal. But the preparation succeeds if we work at a high temperature and mix the silica with carbon. It becomes slightly exothermic if the oxygen of the silica passes into carbonic oxide. The formation of aluminium chloride (from  $\text{Al}_2\text{O}_3$ ) offers an analogous example.<sup>1</sup>

In these reactions the endothermic transformation is possible *owing to an excess of heat furnished by another transformation proceeding at the same time*. By a compensation of this kind *certain endothermic combinations* may be made to take place. Examples :

(1.) We have already seen that  $(\text{H}, \text{I}) = -6.4$  Cal. whilst  $(\text{H}_2, \text{S}) = 4.8$  Cal. Therefore  $\text{H}_2\text{S}$  and  $\text{I}_2$  have no direct action on each other. But it is otherwise if we work in dilute aqueous solution. The heats of solution may then furnish an assisting energy, and the reaction

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<sup>1</sup> It would be necessary besides to take into account the disintegration which the substances undergo at the high temperatures at which these operations are carried out.

\*  $\text{H}_2\text{S.aq} + \text{I}_2 = \text{S} + 2\text{HI.aq}$  takes place, because it evolves about  $-9.5 + 26.4 = 16.9$  Cal.

(2.) "The preparation of the oxygen compounds of chlorine by direct union of the elements would give rise to an absorption of heat. These substances are only formed conjointly with the metallic chlorides by the action of chlorine on the oxides or hydroxides of certain metals. The reaction  $2\text{KOH} + \text{Cl}_2 = \text{H}_2\text{O} + \text{KCl} + \text{KOC}\text{l}$  is exothermic and produces potassium hypochlorite.

These examples will suffice to demonstrate that the existence of certain endothermic compounds is not incompatible with the law of maximum work: they are formed in reactions where the total effect is exothermic. Besides, these compounds are very unstable, and if their formation only succeeds by indirect means their decomposition is generally easily brought about and is often even spontaneous.

The difficulty becomes more serious when we try to interpret those reactions which in their entirety are endothermic. Amongst those there are some which do not fall within the application of *Berthelot's* principle, because they can only be brought about at very high temperatures or under the influence of a foreign energy. Such, for instance, are the preparation of carbon disulphide, the formation of acetylene in the voltaic arc; further, those syntheses by reduction which take place under the influence of light in the green parts of plants (formation of carbohydrates).

But there are also endothermic reactions which can take place spontaneously and without the aid of any external energy. For example:

(a.) Many heats of solution are negative. Sodium chloride, notably, absorbs 1.1 Cal., and its affinity for water is such that a mixture of salt and ice liquefies by absorbing, besides the heat of solution of the salt, the latent heat of fusion of the ice. The affinity which brings about the

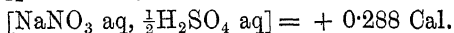
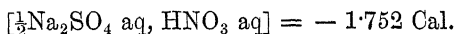


intimate mixture of the molecules must always be obeyed, whatever be the energy used up in the disintegration.

- (b.) Changes which go on in dilute solutions frequently give rise to a negative thermal effect. As instance of this we may take the equation already quoted in the chapter on neutralisation phenomena (page 163):



I would here urge a comparison of the two following equations, which have been experimentally established by *Thomsen*:



Starting with two initially different systems, these reactions lead to the same final equilibrium; and this equilibrium becomes established whatever be the thermal sign of the transposition which takes place. The thermo-negative reaction is, therefore, quite as normal as the thermo-positive.

In spite of these grave objections, *Berthelot* has not abandoned the principle of maximum work. On the contrary, he maintains his first statement, but limits its application to phenomena of a *purely chemical nature*. But it very often happens that the quantities of heat of purely chemical origin are heavily masked by thermal effects due to physical phenomena which take place at the same time as the chemical changes. Before we can class a reaction as essentially endothermic and consequently exceptional, we must, therefore, eliminate from the gross result of the calorimetric experiment, the secondary effects which correspond to external work, to change of state (fusion, volatilisation), and to the intervention of the solvent (heat of solution). With these eliminated we should have a corrected heat of reaction, referred to the solid state, and generally in agreement with the principle

These theories of *Berthelot* are probably partly true and must be taken into consideration. I prefer, however, a thermodynamical solution of this problem because it is more general and more profoundly scientific. Unfortunately, this solution is based on the subdivision of the total energy of a system into available energy (susceptible of being transformed into work) and unavailable energy (capable of manifesting itself only in the form of heat), and on a series of theorems of which it is impossible to give any idea in these 'Outlines of Physical Chemistry.' I can, therefore, only give the conclusions of this special study and say that, according to thermodynamics, the majority of reactions must take place with evolution of heat—in conformity with *Berthelot's* principle; but in certain special cases, notably changes at high temperatures or between diluted substances (gaseous or dissolved), the normal thermal effect may be negative.

The law of maximum work has not, therefore, the value of a principle. It is only a more or less general rule to which we know and foresee many exceptions. In order the better to sustain this conclusion it will be well to recall MAUPERTUIS'S PRINCIPLE (Le Chatelier's theorem) which states that: *any change in the factors of equilibrium from outside is followed by a reverse change within the system.* In thermo-chemistry we translate this to: if, by a change of temperature, we disturb the equilibrium of a system,<sup>1</sup> we give rise to a transposition whose thermal effect is opposed to the change of temperature. In cooling the system we favour exothermic exchanges; on the other hand, on heating we favour endothermic transpositions. These latter appear, therefore, in the natural order of things, and seem necessarily to be realised especially at a high temperature.<sup>2</sup>

<sup>1</sup> The question is, for example, the equilibrium of a reversible reaction:  $AA_1 + BB_1 \rightleftharpoons AB + A_1B_1$ .

<sup>2</sup> The formation of acetylene in the path of the electric arc in an atmosphere of hydrogen may serve here as an example. Amongst

## II. ELECTRO-CHEMISTRY

Any form of energy can be expressed by the product of two factors, one representing the *quantity*, the other representing the *intensity*. When an object is raised to a certain height above the ground, the *potential energy* which it acquires is expressed by  $p \times e$ , i.e. the weight of the object (intensity of the resistance overcome) multiplied by the height through which the object has been raised. If the object be allowed now to fall, it arrives at the ground with the velocity  $v$ , and its *kinetic energy* is expressed by  $\frac{mv^2}{2}$ , where  $m$  denotes its mass. We know that  $\frac{mv^2}{2}$  is equivalent to  $p \times e$ .

The increase of energy which a body experiences on having its temperature raised through a certain number of degrees is equal to the caloric capacity of the body (quantity) multiplied by the rise in temperature (intensity).

In the same way, to determine the energy developed by an electric current we must consider the quantity of electricity which passes and its loss of tension or fall of potential.

OHM'S LAW.—Let us consider the part of the conductor between A and B.



The *intensity* of the current, that is to say, the *quantity of electricity*,<sup>1</sup> which passes through any section whatever  $c$ , in one second, is proportional to the active electromotive force<sup>2</sup> and inversely proportional to the *resistance*

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the metallurgical transformations brought about at high temperatures, many are endothermic.

<sup>1</sup> It may be mentioned that the term *current-intensity* or *current-strength* is the quantity-factor of electrical energy.

<sup>2</sup> That is to say, proportional to the fall of potential between A and B.

offered by the portion of the conductor under consideration :

$$C = \frac{E}{R}$$

JOULE'S LAW.—The electrical *energy* dissipated per second between two points on a conductor is expressed by the product of the current-intensity (or current-strength) by the loss of electromotive force :

$$H = C E,$$

or substituting  $C R$  for  $E$  :

$$H = C^2 R.$$

In order to find numerical expressions for  $C$ ,  $E$ , and  $R$ , we must refer them to well-defined UNITS. These units belong to the C.G.S. system, and are so chosen that the *unit of electrical energy* is equivalent to ten million ergs (erg = dyne  $\times$  centimetre). In other words, under the influence of unit potential, a conductor offering unit resistance allows a current of unit strength to pass through. In one second, therefore, a quantity of electricity is spent whose energy  $C E$  is equal to  $10^7$  ergs.

The theoretical definition of the units is derived from electrostatic and electromagnetic phenomena. As this definition is not of particular importance to us here, we may pass it over in silence and go on to the values of the practical units actually in use.

The unit of *potential* or of electromotive force is called the *volt*, and is so chosen that the potential of a Daniell-Fleming element is 1.072 volts.

The unit of *resistance* is the *ohm*. A column of mercury 1.063 metre long and 1 square millimetre section at 0°C. offers a resistance of one ohm (for the legal ohm the column is only 1.060 metre, and for *Siemens's* unit it is 1 metre).

The unit of *current-strength* is called the *ampère*, and is the strength of a current which passes along a conductor whose resistance is one ohm, under the action of an

electromotive force of one volt. When the current-strength is one ampère the unit of *quantity* passes in one second, and this unit is called one *coulomb*.

When one *coulomb* experiences a fall of potential of one *volt*, then a quantity of electricity equivalent to  $10^7$  ergs is transformed into some other form of energy (heat, light, motion, chemical energy, &c.).

A small calorie is equivalent to about 427 gram-metres, or better (according to Rowland, at the temperature  $18^\circ$ ) to 41,830,000 ergs.

Volt  $\times$  coulomb, that is, the *unit of electrical energy*, is equal to  $10^7$  ergs, and equivalent to 10,210 gram-centi-metres or 0.24 *calorie*.

**FARADAY'S LAW.**—Bodies which allow electricity to pass through them may be divided into two classes. *Conductors of the first class*, such as the metals and certain varieties of carbon, &c., transmit the electric current without suffering any chemical change. As a rule their conductivity diminishes as the temperature rises.

*Conductors of the second class*, or *electrolytes*, only transmit the current through the intervention of a chemical decomposition. Their conductivity, on the contrary, increases with the temperature. To this group fused or dissolved salts belong as well as bases and acids in aqueous solution. The effect of the passage of the current is to decompose these substances into their *ions*. The *cation* which is of an electropositive nature moves *with* the current and separates at the negative electrode or cathode. The anion moves in the opposite direction and is separated at the anode. The following are some examples of electrolytic decomposition:

	Cation	Anion		Cation	Anion
KCl	K	Cl	$K_4FeCy_6$	$K_4$	$FeCy_6$
$K_2SO_4$	$K_2$	$SO_4$	$K_3FeCy_6$	$K_3$	$FeCy_6$
$KC_2H_3O_2$	K	$C_2H_3O_2$			

The ions separated by electrolysis do not always remain free, but frequently react with the electrode or with the solvent.

*Faraday's law* concerning the phenomena of electrolysis states that, *when equal QUANTITIES of electricity pass through different electrolytes, equivalent quantities of these electrolytes are decomposed.* The *equivalent*<sup>1</sup> of an ion is equal to its atomic weight divided by its valency. Suppose that in the circuit of an electric current we place solutions of silver nitrate, copper sulphate, and antimony trichloride, we find that the elements or radicals separated are in the following proportion :

108 of silver,	62 of NO <sub>3</sub>	$\left\{ \begin{array}{l} \text{The metals are deposited} \\ \text{on the cathode. The acid} \\ \text{radicals generally react on} \\ \text{the solvent water and evolve} \\ \text{an equivalent quantity of} \\ \text{oxygen.} \end{array} \right.$
$\frac{63.3}{2}$ of copper,	$\frac{96}{2}$ of SO <sub>4</sub>	
$\frac{120}{3}$ of antimony,	35.5 of Cl	

- The electro-chemical equivalent of an element is subject to the same variations as its valency. Thus for copper we have  $\frac{63.3}{2}$  or 63.3, according as the copper is present in the compound in the cupric or cuprous state.
- From the ferrous and ferric salts we get the equivalents  $\frac{56}{2}$  and  $\frac{56}{3}$  for iron. In potassium ferrocyanide the equivalent of the negative radical is  $\frac{\text{FeCy}_6}{4}$ , whilst in the ferricyanide it is  $\frac{\text{FeCy}_6}{3}$ .

Let us now return to the electrical units and see how they are applied to electrolytic phenomena. *Kohlrausch* and *Lord Rayleigh* have found that a current of one ampère acting for one second on a silver solution deposits 0.001118 gram of silver on the cathode. One coulomb therefore sets free the 96540th part of an equivalent of

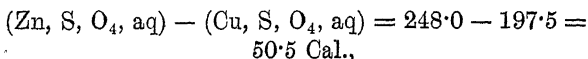
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<sup>1</sup> The term *equivalent* has been used in most of our theories. We meet it here for the third time, but this time it has a profound theoretical meaning.

silver, or the same fraction of the equivalent of any other element or radical. *The electrolytic transportation of one gram-equivalent corresponds, therefore, to the passage of 96,540 coulombs.*

*Remark.*—*Faraday's law* only takes one of the factors of electrical energy into account, namely, the *quantity*, and leaves the other factor—the fall of potential—entirely out of the question.

This relationship between the current and the amount of chemical decomposition holds not only for cases of electrolysis, but is also true for those reactions by which electricity is produced, and gives us a ready means of calculating *the electromotive force of batteries*. In *Daniell's element*, for instance, we have a zinc plate immersed in a solution of zinc sulphate and a copper plate immersed in a solution of copper sulphate, the two solutions being separated by a porous pot. The ultimate chemical reaction which takes place is the replacement of copper by zinc:  $\text{CuSO}_4 + \text{Zn} = \text{ZnSO}_4 + \text{Cu}$ , and for each gram-atom of zinc dissolved there is an evolution of 50.5 Cal. :



and for an equivalent of zinc dissolved 25,250 small calories are evolved.

If this energy were entirely converted into electricity we should obtain  $\frac{25,250}{0.24} = 105,204$  *units of electrical energy* (because  $0.24 \text{ Cal.} = \text{volt} \times \text{coulomb}$ ). But we know from *Faraday's law* that the *quantity* of electricity produced in this case is 96,540 coulombs. The energy developed by the battery will, therefore, be  $96,540 \times E$ ,  $E$  being the electromotive force, and so we get the equation :

$$96,540 \times E = 105,204$$

from which we deduce

$$E = 1.09 \text{ volt},$$

- a number which does not differ very much from that found for this element.

The energy of a battery is necessarily proportional to the quantity of heat evolved in the chemical reaction. But the agreement between the calculated electromotive force and that found by experiment is not always very close. Certain elements when in action become hot, because the chemical energy is not completely converted into electricity (their electromotive force diminishes when the temperature is raised). Other elements which become cold when in action absorb heat from the surrounding medium and give a higher electromotive force than the calculated one (their electromotive force increases as the temperature is raised (*von Helmholtz*)). We even know some elements in which no real chemical transformation takes place; these are the so-called *concentration cells*,<sup>1</sup> and the following are three examples:

Concentrated zinc amalgam .....	Solution of zinc sulphate .....	Weak zinc amalgam
Concentrated cadmium amalgam .....	Solution of cadmium iodide .....	Weak cadmium amalgam
Silver .....	Concentrated (0.1 normal) solution of silver nitrate .....	Dilute (0.01 normal) solution of silver nitrate .....
		Silver

According to *Nernst* the electromotive force of this last-mentioned cell at 18° is 0.055 volt. Its activity is due to the tendency of the two solutions to equalise their concentrations. The dilute solution dissolves some metal from one electrode, and the concentrated solution deposits an equal quantity on the other electrode. Whilst the Ag ion, carrying the positive electricity, passes in the direction from the dilute to the concentrated solution, a corresponding

<sup>1</sup> The electrical energy furnished by these cells is *generally* only a transformation of heat energy derived from the surrounding medium.



quantity of the  $\text{NO}_3$  ion goes in the reverse direction, and these changes take place until the two solutions are of uniform concentration. It is to be noted that neither the quantity of metal nor of silver salt suffers any change.

In the other two cases mentioned the action is due to the tendency of the two amalgams to equalise their concentrations.

A theory of the action of these cells has been proposed by *Nernst*, and is to be found in *M. Le Blanc's* 'Elements of Electro-chemistry,' English translation by *Whitney*.

#### APPARATUS AND METHODS

Having given these general statements we shall now pass on to some of the practical methods in which electro-chemical principles are involved. It cannot be expected that we should here enter into a detailed description of all the apparatus of any importance, and so we shall confine ourselves only to the most essential operations.

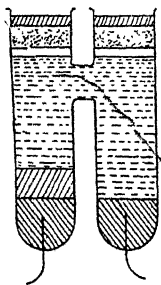


FIG. 38

Perhaps the most important auxiliary apparatus of the electro-chemical laboratory are the STANDARD CELLS, such as the *Daniell-Fleming*, the *Gouy*, and the *Latimer-Clark*.

This last is of the form shown in fig. 38. Two tubes, into the bottoms of which are fused two platinum wires, are connected by a lateral tube. Into one of the tubes an amalgam of nine parts of mercury and one part of zinc is poured (in the molten condition), and into the other some mercury is placed, and this is covered with a mixture, in the form of a paste, of mercurous sulphate, mercury, and zinc sulphate made up with a concentrated solution of zinc sulphate. The whole of the apparatus is then filled with this same solution. The tubes are then hermetically

sealed with paraffined corks and blackened on the outside to avoid the action of light. The electromotive force of a *Clark* at  $15^{\circ}$  is 1.4384 volt. As the temperature rises the electromotive force decreases by 0.001 volt per degree.

*W. Ostwald* recommends the following *one volt element* which has a very small temperature-coefficient. The arrangement of the cell is shown in fig. 39, and it consists of zinc amalgam, solution of zinc chloride (density 1.409), mercurous chloride, and mercury. A more dilute zinc solution produces a current of higher potential, and a more concentrated one gives a lower potential. The element is compared with a standard *Clark*, and water or zinc chloride added until the potential is exactly one volt. The temperature-coefficient is smaller than +0.00007 (the electromotive force increases very slightly with the temperature).

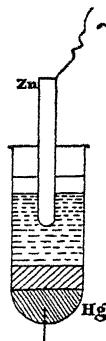


FIG. 39

**SOURCES OF ELECTRICITY.**—In order to obtain a current of low intensity use is made of one or more *Leclanché elements*, the electromotive force of which is 1.2 to 1.3 volt and fairly constant. For stronger currents which are to be used for a considerable time accumulators render the best service. Thermo-electric piles might be used advantageously, but the majority of these are too easily destroyed by superheating. The new *Gulcher pile*, however, seems not to be so easily overheated.

For a description of conductors, keys, contacts, commutators, &c., works on Electricity must be consulted; and here we shall pass on to MEASUREMENT INSTRUMENTS.

The *tangent galvanometer* may be used for directly determining the intensity of fairly strong currents.

The ordinary *galvanometer* reveals the presence and the direction of a current, and within certain limits gives indications of the intensity of the current. In electro-chemical work the sensitiveness of the instrument is

increased by magnifying the movements of the needle. For this purpose a long light glass needle, blackened at its extremities, is fixed on to the astatic system. For delicate measurements a *mirror galvanometer* should be

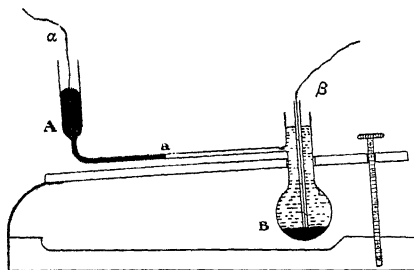


FIG. 40

used; the construction and methods of working of this can be found in any text-book on physics.

*Lippmann's* MERCURY ELECTROMETER is one of the most useful instruments. It may be graduated and used for directly determining potential-differences (up to a maximum of 0.1 volt). It is generally employed to show equilibrium of potentials. *Ostwald* has devised the two adaptations of it shown in figs. 40 and 41 for electro-chemical work.

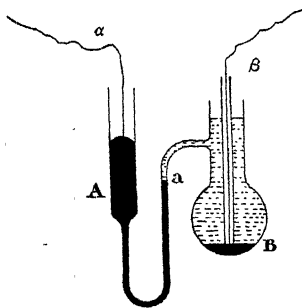


FIG. 41

The instrument consists of the vertical tube A which connects with the reservoir B by means of a narrow tube, whose internal bore must not be greater than 0.5 mm. The tube A contains a column of mercury which by its weight penetrates into the narrow tube and there meets a capillary column of dilute sulphuric acid (1 vol. acid and

- 6 vol. water). The reservoir B contains dilute sulphuric acid, but has a layer of mercury in the bottom. Two platinum wires  $\alpha$  and  $\beta$  (the latter being separated from the sulphuric acid by means of a glass tube) are used for completing the circuit in the apparatus or for putting it in the circuit of a current. When the apparatus is closed on itself (by  $\alpha$  and  $\beta$  being joined) the mercury in the capillary tube takes up a position of equilibrium which is the zero of the apparatus. If the apparatus be now interposed in a circuit, there will be a potential-difference  $e$  between  $\alpha$  and  $\beta$ , and the meniscus of the mercury will be displaced and take up a new position of equilibrium. The length of capillary tube along which this displacement occurs depends on the value of  $e$ , and within narrow limits may be used as a measurement of the potential-difference.

N.B.—The displacement of the mercury is only a secondary phenomenon and is caused by a change which takes place in the surface tension of the metal. In order to maintain the meniscus of the mercury perfectly clean,  $\alpha$  must only be connected with a negative pole, and the cathodic polarisation must never exceed 1 volt (otherwise hydrogen could be evolved at  $\alpha$ ).

The instrument is best read by means of a not very powerful microscope furnished with a micrometer-ocular. *Lippmann's* electrometer is, however, more often used for determining the equilibrium of potentials in compensation methods which we shall very shortly come to.

### *Measurement of Electromotive Force*

There are certain direct methods relying on the use of a galvanometer or of an electrometer, but both for exactness in the results and for simplicity in working it is preferable to reduce the measurement of an electromotive force to the measurement of a resistance, as is done in **POGGENDORFF'S COMPENSATION METHOD.**

In fig. 48, E represents a constant current element the

electromotive force of which must be greater than that of the element to be measured. It is closed by a circuit containing a resistance-box  $R$  and a fixed resistance  $AB$ . The potential-difference at the points  $A$  and  $B$  depends on the electromotive force of the element  $E$  and of the auxiliary resistance  $R$ .

The secondary circuit,  $a\pi\beta$ , contains the element  $\pi$  and a galvanometer or an electrometer. One of the extremities  $a$  is fixed at  $A$ , whilst the other can slide along the graduated resistance  $AB$  by a movable contact  $\beta$ .

If the movable contact is at the point  $A$ , then no current will be sent through the branch  $a\pi\beta$  by  $E$ . But as  $\beta$  is moved to the right the difference of potential between the

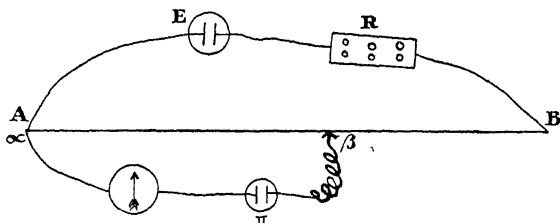


FIG. 42

points  $a$  and  $\beta$  becomes greater, and the current which passes through  $a\pi\beta$  increases in intensity. If the element  $\pi$  be now put in opposition to this current and if  $\beta$  be moved along  $AB$ , when it reaches a certain point the galvanometer will show that no current is passing through the branch  $a\pi\beta$ , so that the opposite potentials are exactly equal. If equilibrium of the potentials takes place, when the element  $\pi$  is in the circuit, when the movable contact is at the point  $\beta$  of the resistance  $AB$ , and if the same is the case when the contact is at  $\beta_0$  with a standard element  $\pi_0$  in place of  $\pi$ , it is evident that the electromotive forces of the two elements are as the lengths  $a\beta$  and  $a\beta_0$ . The equation  $a\beta : a\beta_0 = e : e_0$  contains only one unknown term

$e$ , and therefore this can be calculated in terms of  $e_0$  (the electromotive force of the standard element).

In practice, the resistance of  $AB$  must be fairly large. It generally consists of a board fitted with 21 metallic pins which may be connected above with a circuit and which are connected underneath with each other by resistances of 10

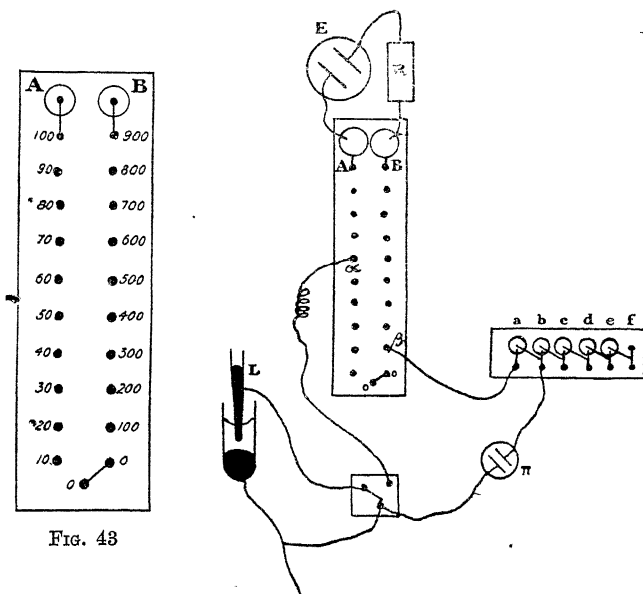


FIG. 43

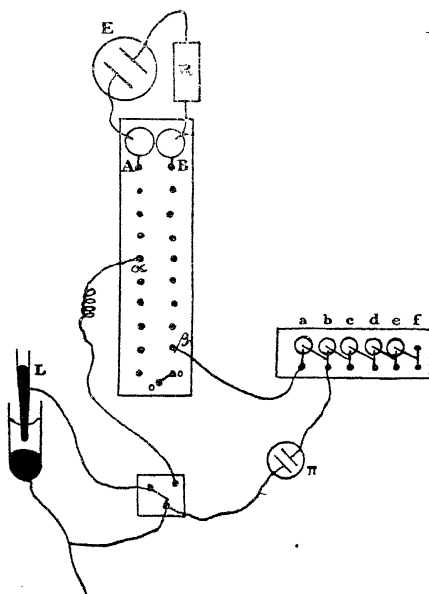


FIG. 44

or of 100 ohms, as indicated in fig. 43. The two pins marked 0 are connected by a thick copper wire.

This total resistance of 1,000 ohms, as well as the auxiliary resistance  $R$ , is placed in circuit with a *Leclanché* element  $E$ , as shown in fig. 44.  $R$  is so modified that a difference of potential of 1 volt exists between  $A$  and  $B$ .<sup>1</sup> Between the pins 0 and 0 there is no difference of potential,

<sup>1</sup> In order to do this a branch circuit containing an electrometer and a standard 1 volt cell is inserted between  $A$  and  $B$ , and the

since they are directly connected with a thick wire. But as we go towards the right or towards the left the potential-difference increases. If we consider, for example, the pins 100 and 60, we find a difference of  $0.1 + 0.06$  or  $0.16$  volt.

Suppose now that in the branch circuit (fig. 44) we have:

1. The element  $\pi$  under examination, in opposition to, the principal current coming from  $E$ .
2. A *Lippmann* electrometer,  $L$ .
3. If necessary, one or more standard 1-volt elements,  $a, b, c, d, e, f$ , in opposition to the element  $\pi$ .
4. A commutator by which the electrometer can be closed on itself or by which the circuit can be closed by interposing the electrometer.

The ends  $\alpha$  and  $\beta$  of the secondary circuit are so connected on the resistance  $AB$  that when the circuit is closed through the electrometer the mercury remains in its position of equilibrium. One succeeds in this after a few trials.

If this takes place when  $\alpha$  and  $\beta$  are at 60 and 100 respectively as in the figure, then the electromotive force measured is  $1.16$  volt, because it is necessary to take the standard 1-volt element  $a$ , which is in opposition to  $\pi$ , into consideration.

### MEASUREMENT OF RESISTANCE :

#### *Wheatstone Bridge Method*

The arrangement of the *Wheatstone bridge* is diagrammatically represented in fig. 45. At the points  $A$  and  $B$  the potentials are  $P$  and  $P'$ , and two points  $C$  and  $D$  having the same potential  $p$  are connected by the bridge (in which there is a galvanometer); and let us suppose that the resistances of the four branches thus formed are  $r$  and  $r'$ ,  $R$  and  $R'$ .

---

standard cell is so arranged that its current is opposed to the current from  $E$ . The resistance  $R$  is then altered until the electrometer denotes potential-equilibrium at  $A$  and  $B$ .

Then, according to *Ohm's law*, in the conductors  $A C B$  and  $A D B$  we have :

$$C = \frac{P-p}{r} = \frac{p-P'}{r'},$$

$$C' = \frac{P-p}{R} = \frac{p-P'}{R'}.$$

Therefore,

$$\frac{r}{R} = \frac{r'}{R'}.$$

Since the points  $C$  and  $D$  are at the same potential, there will be no current in the bridge, and the galvanometer will show no deflection. Conversely, when in such

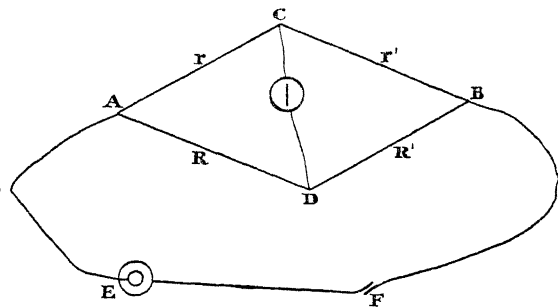


FIG. 45

an arrangement the galvanometer is at zero, the points  $C$  and  $D$  are at the same potential, and the ratio  $\frac{r}{R} = \frac{r'}{R'}$  exists between  $r$ ,  $r'$ ,  $R$  and  $R'$ .

In practice,  $r$  and  $r'$  are known resistances of 1, 10, 100, 1,000..... ohms which can be altered as desired. For  $R$  a resistance-box is used, and  $R'$  is the resistance to be measured. The keys in the resistance-box are then arranged so that the galvanometer indicates no current in the bridge, and  $r$ ,  $r'$ , and  $R$  being known we can calculate  $R'$ .



*Remark.*—The battery circuit A E F B remains open whilst the trials are being made to find the suitable R, and, by means of the spring contact-maker F, the current is allowed to pass through only for a time sufficient to allow galvanometric observations to be made.

The Wheatstone bridge is also useful for making copper or brass wire resistances equal to standard ones. (For details see *Ostwald's* 'Manual of Physico-chemical Measurements,' English translation by *Walker*.)

The MEASUREMENT OF THE INTENSITY OF A CURRENT can be made directly with a tangent or an ordinary galvanometer. With the ordinary galvanometer the deflection of the needle, so long as it is of no great amplitude, is proportional to the intensity of the current. For greater deflections, however, the relation is more complex.

But this direct measurement is not of much use, for we know that  $c = \frac{E}{R}$ , and there are excellent methods for determining both E and R.

### *The Conductivity of Electrolytes*

This subject is of such importance that it has become a sort of 'Leitmotiv' in more than one treatise on theoretical chemistry. The conductivity of electrolytic solutions stands in direct relationship with certain phenomena which have already been discussed, particularly with the osmotic pressure and with the depression of the freezing point. As these properties of solutions have only recently been investigated, it is not hard to understand that they play rather a preponderating rôle in the considerations of modern theorists.

A current can only pass through a salt solution and continue to electrolyse it if it has an electromotive force sufficient to overcome the adverse potentials developed by the polarisation of the electrodes. If, however, the polarisation effects are neutralised or reduced to a negli-

gible minimum, then the smallest electromotive force can produce a current in the solution.

In order to determine the *specific resistance* of a solution in ohms, we consider a cubical mass of the solution, the length of whose side is 1 centimetre. If the resistance of this is  $r$ , then its reciprocal  $\frac{1}{r} = l$  represents the *conductivity*. And if  $l$  be multiplied by the number of cubic centimetres of solution which contains one gram-molecule of dissolved substance, we obtain the *molecular conductivity*, that is, the conductivity which we should observe if the quantity of solution containing one gram-molecule of dissolved substance were placed between two large electrodes 1 centimetre apart.

In order to apply these definitions let us take a fiftieth normal solution of potassium chloride (74.59 grams in 50 litres). According to *Kohlrausch*<sup>1</sup> the *specific conductivity* is 0.002244, and the *molecular conductivity* therefore  $0.002244 \times 50,000 = 112.2$ . These numbers are for 18°; at 25° the molecular conductivity is 129.7.

<sup>1</sup> *Instruments*.—Polarisation effects can be avoided, as *Kohlrausch* has discovered, by using an alternating current of high frequency. The apparatus used is represented diagrammatically in fig. 46, and consists essentially of a Wheatstone bridge in which the galvanometer is replaced by a telephone and, in addition, a small induction-coil B of very rapid vibration, which serves to transform the current derived from the battery P. Those coils constructed for medical use are admirably adapted for this work.

The resistance-box R contains resistances of 1, 10, 100, 1,000..... ohms, and is used for putting in *ac* a resistance of about the same size as that of the electrolytic cell S.

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<sup>1</sup> *Kohlrausch* measures resistances in *Siemens's* units. Nevertheless we shall continue to use the numbers 0.002244 and 112.2 as if they were based on a resistance measured in ohms, and yet the comparativeness of our results will hardly be impaired.

The telephone<sup>1</sup> is placed in the bridge  $c d$ , and  $d$  is a movable contact which slides along the graduated resistance  $a b$ .

This resistance  $a b$  generally consists of a platinum-iridium wire about 0.2 mm. in diameter and 1 metre long, stretched along a board which is provided with a millimetre scale. An alloy of copper and manganese, or one of copper and nickel, may equally well be used for this resistance.

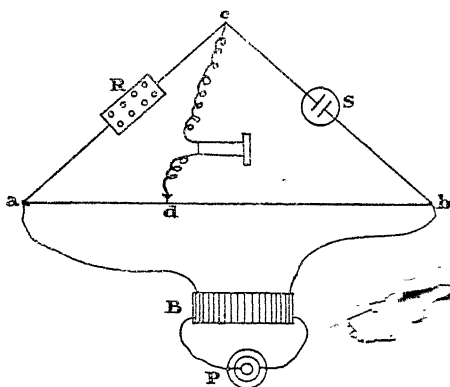


FIG. 46

As the resistance of solutions varies within rather wide limits, the form of the cell  $s$  must be modified to suit the circumstances. For measurements where the conductivity is small the form shown in fig. 47 is used, but in those cases where the conductivity is fairly large the form shown in fig. 48 should be used. The electrodes, which have a diameter of 2 to 4 centimetres, are made of platinum and should be covered with a layer of platinum-black by electrolysing a dilute solution of hydrochloro-platinic acid

<sup>1</sup> The choice of a suitable telephone is of the very greatest importance (under the circumstances a galvanometer cannot be used).

between them.<sup>1</sup> The conducting wires are soldered on to the electrodes, and are protected from contact with the solution by means of a rubber or glass tube.

METHOD.—The *capacity of the electrolytic cell* is first determined, which is done by introducing a solution of known specific conductivity (for example, a  $\frac{1}{50}$  normal solution of potassium chloride). After starting the coil the movable contact is moved along the graduated resistance  $a b$  (fig. 46) until the telephone becomes silent, or at least

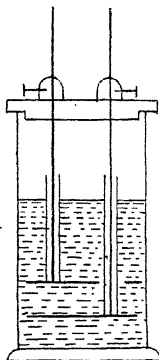


FIG. 47

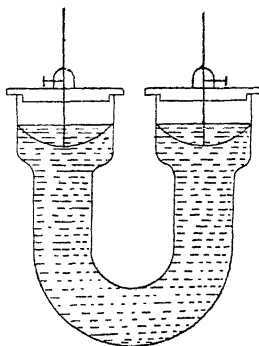


FIG. 48

until the maximum silence-point is reached. At this point the resistances are in the following ratio:

$$R : a d = s : d b.$$

For the resistance wanted, therefore, we have:

$$s = \frac{R \cdot d b}{a d}$$

and for the conductivity:

$$\frac{1}{s} = \frac{a d}{R \cdot d b}.$$

---

<sup>1</sup> The object of this precaution is to increase the surface of the electrodes and thus minimise polarisation effects, which is particularly important for the distinctness of the telephone.

But as we are working with a solution of known specific conductivity  $l$ , we have the relation

$$l = k \times \frac{a d}{R \cdot d' b},$$

from which  $k$  can be calculated, and that value is called the *capacity* of the electrolytic cell employed. This capacity is the factor by which all the direct observations made with this cell must be multiplied so as to bring the specific conductivities into accord with our definition.

If now the same cell be filled, without altering the distance between the electrodes, with a solution of unknown conductivity, and the point  $d'$  found at which the telephone is silent, then we get the *new value*

$$\frac{1}{S'} = \frac{a d'}{R' \cdot d' b},$$

and multiplying by  $k$  we find the *specific conductivity* wanted. The specific conductivity multiplied by  $v$  (the number of cubic centimetres in which one gram-molecule of substance is dissolved) gives the *molecular conductivity*:

$$\mu = k \cdot \frac{v \cdot a d'}{R' \cdot d' b}$$

*Remarks.*—1. In practice, it is common to refer the conductivity, not to the molecular weight, but to the equivalent of the dissolved substance.

2. The *conductivity of electrolytes* generally increases with the *temperature* (probably on account of the increased mobility of the ions). However, a series of substances is known which behave in the opposite manner. Certain acids, such as sulphuric, orthophosphoric, and hydrofluoric acids, belong to this series, and they are all characterised by a particularly high heat of neutralisation.<sup>1</sup>

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<sup>1</sup> We admit that the hydrolytic dissociation of these acids takes place exothermically. Now, according to the principle laid down on p. 181, an elevation of temperature must give rise to an endothermic

3. The *molecular conductivity* increases with the *dilution* up to a maximum which, in the case of good conductors, can be practically attained and corresponds to a solution of one equivalent in about 2,000 litres of water.

The following table gives some *molecular conductivities* at 18° from observations by *Kohlrausch* :

Dilution	KCl	NaCl	LiCl	$\frac{1}{2}$ BaCl <sub>2</sub>	$\frac{1}{2}$ K <sub>2</sub> SO <sub>4</sub>	$\frac{1}{2}$ MgSO <sub>4</sub>
1 litre	91.9	69.5	59.1	65.8	67.2	27.0
10 litres	104.7	86.5	77.5	86.1	89.7	47.4
100 "	114.7	96.2	87.5	100.6	109.8	71.5
1,000 "	119.3	100.8	91.2	109.2	120.7	93.5
10,000 "	120.9	102.9	94.3	112.6	124.9	103.4
50,000 "	121.7	102.8	95.5	114.4	126.6	105.2
100,000 "	121.6	102.4	96.5	114.2	127.5	105.6

The increase in the conductivity with dilution varies according to the nature of the salt. The variation is small for salts formed of two monovalent ions, greater for salts of the type BaCl<sub>2</sub>, and still greater for those of the type MgSO<sub>4</sub>.

4. The *maximum molecular conductivity* ( $\mu_{\infty}$ ) of an organic acid may be deduced from an experimental study of its sodium salt. But the value for  $\mu_{\infty}$  may also be obtained from the following data valid at 25° :

For an acid containing 12 atoms in the molecule  $\mu_{\infty} = 358$

"	"	15	"	"	356
"	"	18	"	"	354
"	"	22	"	"	352
"	"	25	"	"	351
"	"	30	"	"	350

For acetic acid  $\mu_{\infty} = 364$ , for propionic acid 359, and for benzoic acid 356.

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modification of the equilibrium, or, what is the same, a decrease of the dissociation. Consequently, there will be a diminution in the conductivity which more than compensates for the increased mobility of the ions.

5. For organic acids, *Ostwald* has found a regularity which may be made use of for determining their basicity and even their molecular size. The equivalent conductivity of the sodium salt of a monobasic acid increases by ten units when we pass from a solution of 32 litres dilution to one of 1,024 litres dilution. For a dibasic acid the increase is twenty units; for a tribasic acid thirty units and so on (always for the same increase of dilution).

Many other regularities have been noticed, but I shall only call attention to

#### KOHLRAUSCH'S LAW (1876)

*Kohlrausch* has found that the molecular conductivity of neutral salts <sup>1</sup> is composed additively of two factors, one of which depends solely on the nature of the base, and the other on the nature of the acid. This law, it may be noticed, exactly resembles the law of thermo-neutrality, and is in direct correlation with certain of *Hittorf's* considerations (1851).

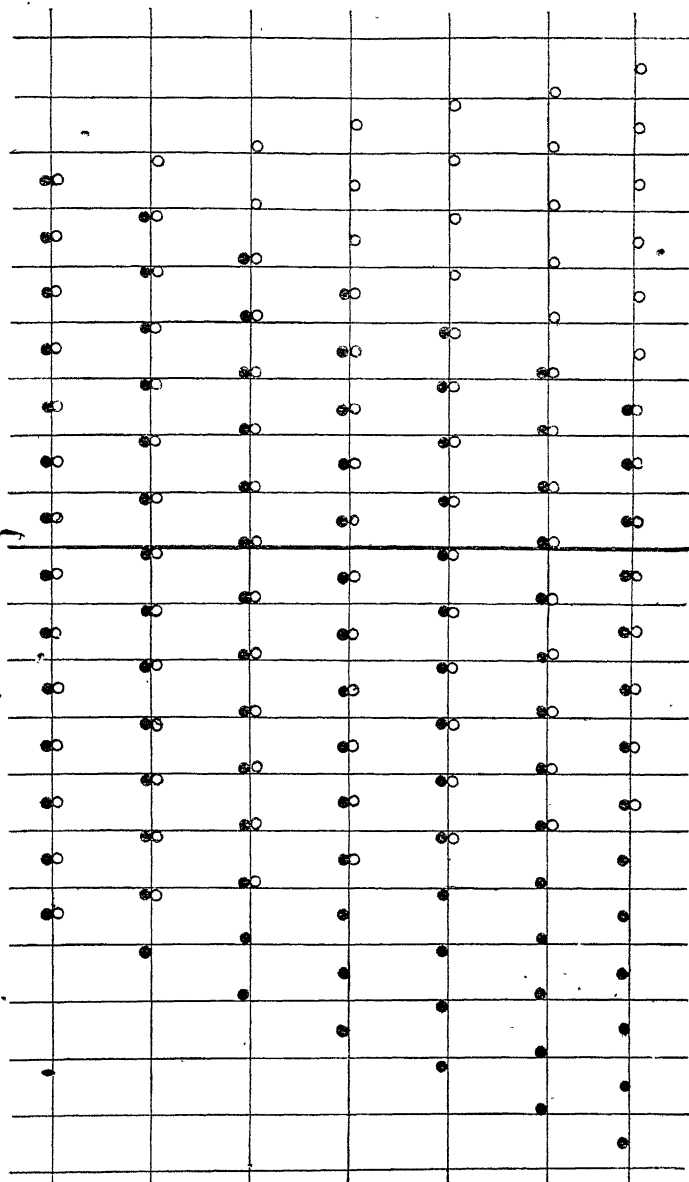
If in an electrolysis the positive and the negative ions migrate at the same speed, the fall in the concentration of the solution is the same at both electrodes. But as this is not generally the case, *Hittorf* suggested that the ions migrate at different speeds, as is indicated in the diagram, fig. 49.

The black points represent one ion, the white circles the other. Under the influence of a current the black ions move to the left, the white to the right, with this difference, that to pass from molecule to molecule the black ions move twice as fast as the white ions. The top row represents the condition of the solution before electrolysis, the following rows successive states during the electrolysis. The vertical line *ab* divides the original condition into two equal parts. At the beginning there are seven black and seven white ions on each side of this line. The last

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<sup>1</sup> In sufficiently dilute solution.

a





row shows six decomposed molecules and eight undecomposed, five of which are to the left of  $ab$  and three to the right. The number of black ions to the left has increased by four (from seven to eleven), whilst to the right the number of white ions has increased by two. The ratio  $\frac{4}{2}$  expresses the RELATIVE RATES OF MIGRATION which we presupposed for the ions.<sup>1</sup>

If now we observe that during the electrolysis of a *dilute* solution of potassium chloride (1 equivalent in 1,000 litres) the concentration diminishes *quasi-uniformly* at both electrodes, then we must conclude that the K and the Cl ions migrate at the same rate. If the molecular

<sup>1</sup> In order to experimentally determine this speed-ratio, it is only necessary to find what concentration change takes place at one of the electrodes. An example will make the method clear. Suppose that a solution of silver nitrate which has been subjected to electrolysis for a certain time has deposited 1.2591 grams of metallic silver, and that a certain volume of the solution taken from just beside the cathode now contains 12.5533 grams of silver, whereas before the electrolysis this same volume contained 13.1426 grams. The solution at the cathode has therefore lost 0.5893 gram of metal and has sent in the direction of the anode an equivalent quantity of the  $\text{NO}_3$  ion. At the same time 1.2591 - 0.5893 = 0.6698 gram of silver has migrated from the solution at the anode towards the cathode. The immigration of the silver is therefore to the emigration of the  $\text{NO}_3$  group as 0.6698 : 0.5893 or as 0.532 is to 0.468. These numbers express the relative rates of migration of the ions of silver nitrate in a fairly strong solution (in dilute solution the  $\text{NO}_3$  ion migrates faster than the Ag ion).

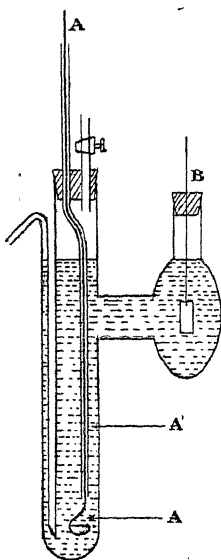


FIG. 50

solution is withdrawn through the side tube and analysed. For details see the original papers of *Hittorf*, *Nernst*, *Loeb*, and others.

conductivity of such a solution is 119.3 (*Kohlrausch* units), then half of this number, namely, 59.7, expresses the CONDUCTIVITY COEFFICIENT of potassium and also of chlorine.

We are now in possession of the key to the system. For, if from the conductivity of the solution of sodium chloride (1 equivalent in 1,000 litres) we subtract the coefficient for chlorine we find the value 41.1 for sodium. By similar deductions the value 32.4 has been found for lithium, and values have also been found for many more ions.<sup>1</sup>

The coefficients thus deduced stand in the same ratio to each other as do *Hittorf's* values for the rates of migration deduced from the changes of concentration at the electrodes. Thus the one method confirms the results obtained by the other.

The study of neutral salts in aqueous solution thus gives us, for a series of *monovalent ions*, the factor known as the *coefficient of conductivity* or often as the *speed of migration*.

*Acids* of the type HCl and HNO<sub>3</sub> have very high conductivities, mostly due to the high speed of the hydrogen ion, as the following shows:

Dilution	HCl	HNO <sub>3</sub>
1 litre . . . . .	278.0	277.0
100 litres . . . . .	341.6	339.5
1,000 „ . . . . .	345.5	342.7

<sup>1</sup> The majority of the numbers here cited are taken from *Ostwald's* book. They have been determined by *Kohlrausch* and refer to the temperature 18°C. and to dilutions 1,000 to 2,000 litres.—At this same temperature, but at infinite dilution, *Kohlrausch* has calculated the following conductivity co-efficients:

For K $u = 60$	For H $u = 290$	For Cl $v = 63$
„ NH <sub>4</sub> $u = 60$	„ $\frac{1}{2}$ Ba $u = 30$	„ I $v = 63$
„ Na $u = 41$	„ $\frac{1}{2}$ Mg $u = 26$	„ NO <sub>3</sub> $v = 58$
„ Li $u = 33$	„ $\frac{1}{2}$ Zn $u = 24$	„ ClO <sub>3</sub> $v = 52$
„ Ag $u = 52$		„ ClO <sub>4</sub> $v = 54$
$u$ denotes the coefficient for the metal		„ C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> $v = 33$
$v$ „ „ „ acid-radical		„ OH $v = 165$

By subtracting the coefficient for chlorine from 345.5 we find the speed of migration of hydrogen 285.8.

For *bases*, *Kohlrausch* has found at 18°C.:

Dilution	KOH	NaOH
1 litre . . . . .	171.8	149.0
100 litres . . . . .	212.4	187.0
1,000 „ . . . . .	214.0	188.0

The conductivity of potash diminished by the coefficient for potassium gives the value 154.8 for hydroxyl.

The relations are not quite so simple for acids and bases containing multivalent ions. Furthermore, there are some more or less difficultly electrolysable compounds whose conductivity is even lower than that of the hydrogen or the hydroxyl which they contain.

Dilution	$\frac{1}{2}\text{H}_2\text{SO}_4$	$\frac{1}{3}\text{H}_3\text{PO}_4$	$\text{C}_2\text{H}_4\text{O}_2$	$\text{NH}_4\text{OH}$
1 litre . . . . .	188.9	29.0	1.2	0.84
100 litres . . . . .	285.5	79.0	13.2	9.20
1,000 „ . . . . .	331.6	96.8	38.0	26.00

In order to reconcile this seemingly anomalous state of things, *Arrhenius*, *Ostwald*, and several other distinguished theorists assume that when an electrolysable compound (acid, base, or salt) is dissolved a DISSOCIATION INTO FREE IONS takes place. For good conductors this dissociation takes place readily, and at a dilution of 1,000 or 2,000 litres it may be assumed to be complete. Sufficiently dilute equivalent solutions must then contain the same number of free ions, and consequently the conductivity of these solutions depends only on the speed of the ions. Indeed, *Faraday's law* teaches us that the electric charge on any ion whatever is a *constant quantity*.

For bad conductors (phosphoric acid, acetic acid, ammonia) the dissociation is only partial and does not take place so readily. As the free ions are not very numerous, the conductivity will be much diminished compared with what it would be if the dissociation were complete.

Admitting this view for the present, we see that the conductivity of a solution will be proportional to the number of free ions which it contains and to the rate of migration of these ions. The expression for *Kohlrausch's law* will therefore not be—

$$\mu = u + v$$

( $\mu$  being the molecular conductivity of a salt at a given dilution, and  $u$  and  $v$  being the speeds of the ions), but—

$$\mu = x(u + v)$$

$x$  being a fractional number which expresses the *degree of dissociation* of the salt.

As the dilution increases the value of  $x$  approaches unity, and at infinite dilution  $x = 1$ , so that

$$\mu_{\infty} = u + v$$

For salts containing monovalent ions the dissociation is practically complete at a dilution of 1,000 to 2,000 litres; and a further increase in the dilution causes the conductivity to become only very little higher. The same holds for certain acids and certain bases: HCl, HNO<sub>3</sub>, KOH, NaOH, &c., and  $\mu_{\infty}$  is known for these substances.

Salts of strong acids with a weak base and of weak acids with a strong base belong to the category of easily dissociable bodies. From their investigation we can deduce the rate of migration of the ions of weak acids and of weak bases, and thus the speed of all ions can be ascertained.<sup>1</sup>

If we possess a complete table of values of  $u$  and  $v$ , we can find, by means of the equations

$$\mu = x(u + v)$$

$$\mu_{\infty} = u + v,$$

---

<sup>1</sup> If from the maximum observed conductivity of, for instance, sodium acetate, we subtract the speed of the Na ion, we obtain the speed of the C<sub>2</sub>H<sub>3</sub>O<sub>2</sub> ion.—By adding to this latter the speed of the H ion we obtain  $\mu_{\infty}$  for acetic acid.

the value of the coefficient of dissociation :

$$x = \frac{\mu}{\mu_{\infty}}.$$

In this equation  $x$  denotes the degree of dissociation of an electrolyte at any particular dilution,  $\mu$  is the molecular conductivity measured at the same dilution, and  $\mu_{\infty}$  is the conductivity calculated for infinite dilution (the sum of  $u$  and  $v$ ). The determination of the electric conductivity of a solution, therefore, offers us a method of ascertaining the degree of dissociation of the dissolved substance.

We shall have occasion later to return to the subject of dissociation in solution.

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### III. THE NATURE OF SALT SOLUTIONS

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THE comparative study of electric conductivities has led us to assume a certain dissociation for dissolved electrolytes.<sup>1</sup> Let us now see if this hypothesis is in thorough agreement with all the characters of salt solutions, and particularly with the exceptional properties which have been referred to in the chapter on 'Osmotic Methods.'

In connection with *osmotic pressure* it has already been pointed out that *van't Hoff's law* is only directly applicable to the majority of organic substances, and in general to substances of a not very well defined chemical character. Strong acids, strong bases, and salts develop an osmotic pressure which is too high, and which is more or less proportional to the number of ions of which the dissolved molecule is composed.

In treating of the density of gases and vapours, and of the application of *Avogadro's hypothesis*, we remarked on an anomaly of the same kind. Certain substances, such

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<sup>1</sup> For the present we shall consider only aqueous solutions; especially as the dissociation is most distinctly manifested in aqueous solution.

as ammonium chloride, phosphorus pentachloride, ammonium carbamate, &c., in the gaseous state occupy a volume which is  $m$  times greater than that expected, and, consequently, under normal volume condition they exert a pressure which is  $m$  times too great. In order to explain this we assumed that in passing into the gaseous state the molecule is decomposed into smaller particles.

An analogous assumption can be made to explain the irregularity under discussion. If a dilute aqueous solution develops an *osmotic pressure*  $i$  times too great,<sup>1</sup> it is probable that the solution contains  $i$  times more dissolved particles than would be expected from the unitary formula of the substance dissolved.

Thus the exceptions to *van't Hoff's law* lead us to the same hypothesis as we have formulated to explain the conductivity of solutions. And it may be at once added that the agreement between these two classes of phenomena is not only qualitative, but can also be followed quantitatively.

If we take a salt solution of *molecular conductivity*  $\mu$ , and which has an *osmotic pressure*  $i$  times too great, what will be the value of the fractional number  $x$ , expressing the *degree of dissociation*?

The first reply to this question is furnished by *electrochemistry*, because from the determined molecular conductivity we can calculate  $x$  from the equation:

$$x = \frac{\mu}{\mu_{\infty}}.$$

From the *osmotic point of view* it is not any more difficult to ascertain the value of  $x$ . We know to what number of ions the chemical composition of the dissolved substance corresponds, and for the present we may assume (as *Arrhénius* does) that the dissociation consists in a liberation of the ions. Now, if the dissociation were zero,

<sup>1</sup> I.e.  $i$  times the pressure calculated from *van't Hoff's law*.

then there would be  $N$  unitary molecules dissolved in the solution, and the osmotic pressure would be normal. But a certain fraction  $x$  of this number of molecules suffers hydrolytic decomposition, and only  $(1 - x) N$  molecules remain unchanged, whilst the  $xN$  dissociated molecules give  $xN$  times  $n^1$  free ions. The osmotic pressure is, therefore, not determined by  $N$  particles, but by  $(1 - x) N + n x N$  material particles; and as the osmotic pressure is  $i$  times too large we may write

$$i = \frac{(1 - x) N + n x N}{N} = 1 + (n - 1) x.$$

In this equation  $i$  and  $n$  are known and  $x$  can be calculated:

$$x = \frac{i - 1}{n - 1}.$$

As a rule (at any rate for binary electrolytes) the value found for  $x$  by either of these methods is the same.

But as direct osmotic experiments are extremely difficult to carry out, it would be dangerous to make them serve as the basis of a theoretic system.

This would be a serious objection were it not that *a mathematical relation exists between the osmotic pressure of a solution and its boiling and freezing points.*<sup>2</sup> The boiling-point or the freezing-point of a solution being known, we can calculate its osmotic pressure, and so the direct determination of this pressure is quite superfluous. Besides, all the observed facts tend to show that there is a direct connection between osmotic methods and boiling and freezing point methods. Thus, if the osmotic pressure of a solution is *regular*, its rise in boiling-point and its

<sup>1</sup>  $n$  is the number of ions of which the molecule is composed.

<sup>2</sup> See the chapter, 'Theoretical Relations,' on p. 127. There the relationships between osmotic pressure and the vapour tension, the boiling-point, and the freezing-point of a very dilute solution con-

depression of freezing-point can be found from the equations:

$$\frac{\text{rise in boiling-point}}{p} M = E$$

and 
$$\frac{\text{depression of freezing-point}}{p} M = C$$

where  $M$  is the true molecular weight of the dissolved substance. If, on the contrary, the pressure is  $i$  times too large, as is the case with electrolytes, then the rise in boiling-point and the depression of freezing-point become equally exceptional and lead to results for the molecular weight which are  $i$  times too small.

The value found for  $M$  being evidently inversely proportional to the number of particles of matter in solution, we are again led to the equation

$$i = \frac{(1-x)N + nxN}{N} = 1 + (n-1)x$$

and thus we have new methods of determining  $x$ —by means of the boiling-point and the freezing-point.

As the value of  $x$  is independent of the method by

taining  $n$  gram-molecules of substance dissolved in  $g$  grams of solvent, have been given.

We know that  $\frac{f-f'}{f} = \frac{n}{g}$ , and that  $\Delta = E \frac{n}{g}$  ( $\Delta$  being the rise in the boiling-point).

And Arrhénius has shown that—

$$P = h s = \frac{n}{g} R T s.$$

Now, substituting the values of  $\frac{n}{g}$  of the two first equations in this last, we get

$$P = \frac{f-f'}{f M} R T s = \frac{\Delta}{E'} R T s.$$

*N.B.*— $P$  denotes the osmotic pressure;  $M$  is the molecular weight (gaseous) of the solvent;  $\tau$  is the boiling-point of the solvent in absolute degrees.

For cryoscopic phenomena analogous relations can be established.



which it is arrived at, and as the indirect methods have been applied to an enormously large number of substances, we may say that we possess sufficient data to prove that the hypothesis of dissociation is a quasi-certainty.<sup>1</sup>

The *degree of dissociation* depends on several circumstances, but chiefly on the two following :

1. The nature of the dissolved substance. Strong acids, strong bases, and salts which contain a strong acid or a strong base are very easily dissociated. On the contrary, weak acids (such as  $\text{H}_2\text{S}$ ,  $\text{SO}_2$ ,  $\text{C}_2\text{H}_4\text{O}_2$ , &c.), and weak bases (such as  $\text{NH}_3$ ,  $\text{C}_6\text{H}_5\text{NH}_2$ , &c.), and salts which contain neither a strong acid nor a strong base, do not readily dissociate.

2. The concentration of the solution. For substances which dissociate easily the limiting value of  $\alpha$  can be practically attained. A dilution of one gram-equivalent of substance in 1,000 litres of water is generally sufficient to produce quasi-complete dissociation. For more concentrated solutions the value of  $\alpha$  is fractional, as was shown by *Kohlrausch* from the molecular conductivities of solutions of salts, acids, or bases (pages 201 and following).

As to the nature of salt dissociation we can only express some suppositions.

*Sv. Arrhénius* in 1887 declared in favour of the idea of the ABSOLUTE FREEDOM OF THE IONS, and his theory is accepted and expounded by *Ostwald* in his excellent treatise on theoretical chemistry and by *Nernst* in the theoretical introduction which he wrote for *Dammer's* book.

If this theory be accepted, then it is easy to understand the meaning of such terms as 'the rate of migration of the

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<sup>1</sup> For the same solution we can find the degree of dissociation by three different methods : electric conductivity, boiling-point, freezing-point. If these methods could all be carried out at the same temperature, there is no doubt but that they would all give the same value for  $\alpha$ . This, of course, is impossible, and, as the dissociation is a function of the temperature, the values found for  $\alpha$  will not be quite the same.

ions,' 'the electrical capacity of the ions (equal for all),' 'the transportation of the electricity by the ions,' and so on; and scientific language gains in realism and in simplicity. But this simplicity has only an apparent existence, and when we go to the root of the matter discrepancies appear. On this account the champions of the new theory insist on the necessity of not attributing to the free ions the properties of the elements in the massive state. The ion of potassium, for instance, is not to be confounded with the metal of that name. The ion is an isolated atom with an enormous electric charge. The massive metal on the contrary is constituted of a complex assembly of atoms and has no electric charge. In an electrolysis, when the potassium ion is deposited on an electrode to which it gives up its charge, metallic potassium is immediately formed and decomposes the solvent water with evolution of hydrogen.

Without admitting the whole of this theory we must confess that *Arrhénius's* hypothesis interprets admirably a series of phenomena of which we otherwise know neither the significance nor the *raison d'être*.

1. *The law of thermo-neutrality (Hess).*

When two dilute neutral solutions are mixed together no thermal effect is produced. The reason of this is that no reaction takes place.

A solution of potassium chloride, for instance, contains the ions K and Cl; in the same way a solution of sodium nitrate contains the ions Na and NO<sub>3</sub>. When the two solutions are mixed no change takes place, for the ions remain free just as they were before.

The law only applies to sufficiently dilute solutions in which the dissociation is complete or almost so. Concentrated solutions behave in a more or less abnormal manner.

2. *Wet reactions, which are so much used in inorganic chemistry for recognising the nature of a substance, show*

clearly that in aqueous solution IONS have an independent existence.

Silver nitrate gives, with a solution of any metallic chloride, a white precipitate of silver chloride. But if silver nitrate be added to a solution of potassium chlorate or of monochloroacetic acid the silver does not unite with the chlorine. Ferrous salts give a black precipitate with ammonium sulphide, but this same reagent gives no black precipitate with potassium ferrocyanide. From these examples, which might be greatly multiplied, we can see that the reactions take place between ions. A silver solution is not a reagent for chlorine, but for the chlorine ion; ammonium sulphide is a reagent for the ferrous ion. Analytical chemistry is based principally on reactions of double exchange between ions. There are no reagents for such and such an element, but for such and such an ion.

It must be noticed that ions behave in a different manner according to their valency. The iron ion, for instance, behaves in two different ways according as it is derived from a ferrous or from a ferric salt. In the same way the radical  $\text{FeCy}_6$  behaves in different ways according as it is present as a ferrocyanide ( $\text{K}_4\text{FeCy}_6$ ) or as a ferricyanide ( $\text{K}_3\text{FeCy}_6$ ).

These are the most important facts which can be produced in favour of Arrhénius's doctrines, and I shall now devote a few lines to a critical examination of this hypothesis.

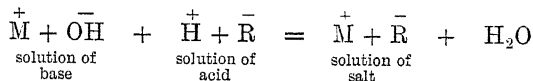
Above everything else we notice that the hypothesis of free ions is in opposition to thermo-chemical observations.

Let us recall that hydrogen and chlorine in uniting evolve much heat, and that the solution of hydrochloric acid gas in water is strongly exothermic.

In spite of this, if the theory of Arrhénius be true, no closer union of the atoms has taken place, for in the solution the dissolved acid is in the state of free hydrogen and chlorine ions. Again, the heat of formation of caustic soda is very large and its heat of solution is by no means negligible; and further, a solution of caustic soda neutra-

lised by one of hydrochloric acid evolves 13·7 Cal. And yet the theory states that the final product contains only dissociated salt:  $\text{Na} + \text{Cl}$ . So that the successive heats evolved, which would seem to indicate a gradual condensation of matter, are leading to the maximum disintegration—to the absolute freedom of the ions. The contradiction is surely evident.<sup>1</sup>

Of all the exothermic effects enumerated above, the new theory only gives a satisfactory explanation of one—namely, the heat of neutralisation. The formation of an equivalent of salt by the interaction of a strong base and a strong acid in dilute aqueous solution is accompanied by an almost constant evolution of 13 to 14 Calories, and Arrhenius explains that the following takes place:



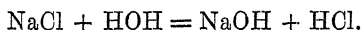
The ions  $\overset{+}{\text{M}}$  and  $\overset{-}{\text{R}}$  (metal and acid radical) after the reaction being free, as before, the only change which has taken place is the union of the ions  $\overset{-}{\text{OH}}$  and  $\overset{+}{\text{H}}$  to form neutral water. Now *water is not an electrolyte*<sup>2</sup> and is, therefore, not dissociated, but is formed with evolution of heat. As there is no other thermal effect, *this* formation of water always corresponds to about the same evolution of heat—about 13 Calories.

The constancy of the heat of neutralisation is thus explained, but *the whole of the thermo-chemical data does not seem to be in accord with Arrhenius's theory.*

<sup>1</sup> This contradiction appears quite as well if we consider the heat of formation of sodium chloride from its elements; 97·9 Cal., leaving out of account the energy dissipated in decomposing the molecules  $\text{Na}_2$  and  $\text{Cl}_2$ . The solution of the salt absorbs only a small quantity of heat. And yet according to the theory this solution actually sets the sodium and the chlorine free, and that without any chemical intervention on the part of the solvent.

<sup>2</sup> Specific conductivity of water slowly distilled in a good apparatus:  $2 \times 10^{-6}$ . Specific conductivity of water distilled *in vacuo*: about eight times less.

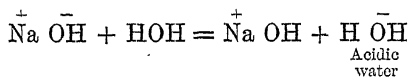
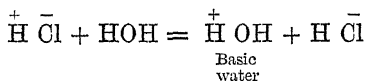
In face of these difficulties I have endeavoured to find whether the hypothesis of free ions is absolutely necessary, and whether another sort of dissociation would not suffice to explain the observed facts. Let us assume for the moment that sodium chloride reacts with water in the following manner :



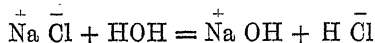
The number of active particles is doubled just as it is according to *Arrhenius's* hypothesis, and consequently the abnormal values found for the osmotic pressure and the correlative data are equally well explained.

But a difficulty presents itself in the fact that it is not only the salt which behaves as an electrolyte; hydrochloric acid and caustic soda possess the same character, and for the factor  $i$  give a value which is almost equal to 2.

In consequence, I propose to bring forward again an old idea, and assume that in a free acid the hydrogen plays the part of a metal and in a free base the hydroxyl is a true acid radical. In this manner the molecules  $\overset{+}{\text{H}} \bar{\text{Cl}}$  and  $\overset{+}{\text{Na}} \bar{\text{OH}}$  have the constitution of salts, and as such they dissociate under the influence of solvent-water :



Comparing these two equations with that which we supposed for the dissociation of sodium chloride :



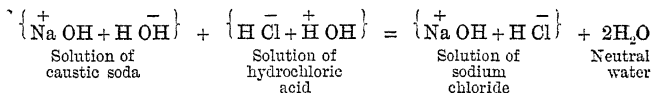
we notice a perfect analogy.

We may further recognise that if in its ordinary state

water is neutral and not an electrolyte, it may, in presence of an acidic or basic molecule, itself become electropositive (basic) or electronegative (acidic).

Now, a molecule of water thus IONISED is different from ordinary water, and becomes active from the point of view of the osmotic pressure, the depression of the freezing point, &c. ; and that is why caustic soda and hydrochloric acid have the same value for  $i$  as sodium chloride has.

From the *thermo-chemical point of view* this theory meets with no difficulty. The neutralisation of a solution of hydrochloric acid by a solution of caustic soda gives rise to the following reaction :



For the neutralisation of the affinities of the base and of the acid, and for the formation of two molecules of neutral water, there is an evolution of 13·7 Calories.

The *law of thermoneutrality, analytical reactions, &c.*, can be equally well explained by the two hypotheses. The explanations already given (pages 213–214) remain as they stand. It is only necessary to replace the free ions by the new products of dissociation and consider that they (the ionised molecules) have a real and independent existence in the aqueous solution.

For the ELECTROLYTIC PHENOMENA we come back to a somewhat modified form of *Grotthus's* hypothesis. The system  $\overset{+}{\text{Na}}\text{OH} + \text{H} \overset{-}{\text{Cl}} + n\text{H}_2\text{O}$  does not form a stable but only a stationary equilibrium. The molecule  $\overset{+}{\text{Na}} \overset{-}{\text{Cl}}$  may be momentarily formed, but only to be broken up again. The result of this is that the sodium and the chlorine ions possess great mobility. The atom Na, for example, is not constantly united to the same OH, nor is the atom Cl always joined to the same H, but these atoms are tossed about from molecule to molecule, and

thus possess all the freedom of movement which is required by the electrolytic phenomena and attributed by *Arrhenius* to the free ions. Electrolysis itself and that function which we have termed the coefficient of conductivity (or speed of the ions) are equally well explained by the two hypotheses. These hypotheses differ only in one point: according to one the ions are atomically free, whilst in the other theory the freedom of the ions is caused by the dissociating action of the water, and by the frequent passages which the ions make from one molecule to another. We thus explain the special rôle played by the water,<sup>1</sup> and as we do not assume any great disintegration, we have the advantage of not coming into conflict with thermo-chemical facts.

### THE MECHANISM OF THE OSMOTIC PRESSURE

I. We shall first take up the theory of *van't Hoff*, as it appears in the interchange of views on the part of this scientist and *L. Meyer* ('*Zeitschrift f. physik. Chem.*' and '*Berichte der deut. chem. Gesell.*,' 1890).

In pure water the molecules  $H_2O$  must be in equilibrium with the surface tension of the liquid and the external pressure. In a solution, on the contrary, the water only occupies a part of the total volume (or, is in a state of expansion); it has, therefore, only to bear a part of the supported pressure, the dissolved substance bearing the other part.

In the determination of an osmotic pressure, therefore, the molecular tension of the water is not the same on both sides of the semipermeable wall, but is greater on the outer side (pure water) than on the inner (solution). The result of this is that the solvent filters in from the outside

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<sup>1</sup> We shall later have occasion to speak of the dissociating action of other solvents, but we may remark that water is the dissociating liquid *par excellence*.

until the partial tension of the water in the solution has become equal to the complete tension of the pure water outside. The cell thus becomes the seat of an increase of pressure which can be measured on the manometer, and which is solely due to the partial tension of the dissolved substance.

This interpretation recalls the laws of mixture and diffusion of gases.<sup>1</sup> It depends, furthermore, on the *kinetic theory of the liquid state*,<sup>2</sup> and attributes to the dissolved (and consequently liquid) molecules the kinetic energy which they would have in the gaseous state. For otherwise we could not understand that the osmotic pressure, caused solely by the partial tension of the dissolved substance, is equal to the pressure which this

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<sup>1</sup> The reader has only to think what the result of the following experiment would be. A cell with rigid walls permeable to hydrogen only is filled with a mixture of hydrogen and nitrogen, and is immersed in an atmosphere of pure hydrogen. We suppose, of course, that the gaseous mixture and the pure hydrogen are under the same pressure.—The result would be that hydrogen would penetrate into the cell and there cause an increase of pressure equal to the initial partial pressure of the nitrogen.

<sup>2</sup> It will not be out of place to give here some brief indications about this theory. The liquid and the gaseous states are connected by a perfect transition (the critical state), and are governed by the same equation (that of *van der Waals*). There is, therefore, no qualitative difference between these two states. A liquid is simply a very concentrated gas; only a small fraction ( $p$ ) of its enormous

internal pressure  $\left( p + \frac{a}{v^2} \right)$  becomes externally manifest, whilst the

rest  $\left( \frac{a}{v^2} \right)$  is equalised by molecular attraction and notably by the

*surface tension*.—When we compress a gaseous mass we diminish the distance between its molecules and thus favour molecular attraction. By applying a sufficiently high pressure we may even make this distance so small that the mutual attraction of the molecules outweighs the kinetic energy of translation—that is to say, that the liquid state becomes realised. The possibility of this transformation depends not only on the pressure applied, but also on the temperature, for this conditions the kinetic energy of the molecules

$\left( \frac{mv^2}{2} \right)$ . This energy is, moreover, independent of the degree of condensation of a substance.



substance would exercise if it were in the gaseous condition (*van't Hoff's law*).

The interpretation which has just been given leaves much to be desired from the quantitative point of view (*Nernst*). We must not forget that the dissolved molecules are under an enormous pressure  $\left(p + \frac{a}{v^2}\right)$ , and that consequently their external pressure, i.e. the osmotic pressure, could not be predicted from the general equation of a gas but could be from *van der Waals's* equation. But according to this latter we should require to find pressures higher than those which have actually been observed.<sup>1</sup> This forms a serious objection, and the problem seems not yet to be definitely solved.

II. As a sequel to *van't Hoff's* interpretation I venture to bring forward another which does not require the kinetic theory of liquids and which is founded only on some ideas already old (perhaps even somewhat antiquated?). If we assume that, in an aqueous solution, the dissolved substance is in the liquid state, and that the attraction attains its greatest value when acting between molecules of different natures, we may reason as follows.

In fig. 51 *a* and *a'* represent two dissolved molecules, and *r* is the radius of their spheres of molecular attraction.

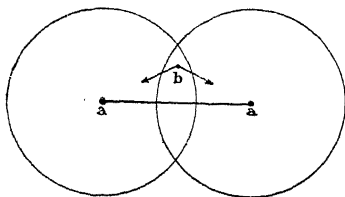


FIG. 51

A molecule *b* of solvent will be attracted both by *a* and *a'*, and the resultant will cause *b* to approach the line joining *a* and *a'*.

By the united action of many molecules of solvent a force will be established which will separate the two dissolved molecules until the distance between them is  $2r$ . The spheres

<sup>1</sup> In the last edition (1898) of *Nernst's* 'Theoretische Chemie' this criticism is omitted.

of attraction will no longer have a common part, and the mutual attraction of  $a$  and  $a'$  will be reduced to a minimum. This takes place as if the dissolved molecules tended to separate from each other as far as they would if they were gaseous.—But it does not suffice to consider two molecules swamped in an excess of solvent, similar to two gaseous molecules in an indefinite vacuous space; for in a solution, the molecules  $a$  and  $a'$  are surrounded on all sides by  $a''$ ,  $a'''$ , .....  $a^n$ , and the condition of equilibrium in such a system is the mutual and equal penetration of the spheres of attraction.

If we now represent an osmotic experiment diagrammatically as in fig. 52, we find on one side of the semipermeable wall an excess of the solvent (B), and on the other side the solution (A) the dissolved molecules of which are equidistant from each other.<sup>1</sup>

Before starting the experiment the semipermeable walls are moistened and the pores filled with pure water. If we admit that there is a great affinity between the molecules

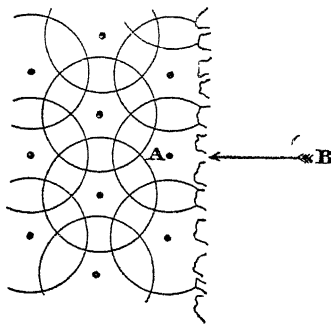


FIG. 52

of water and the material particles of the wall, then there must exist a disjunctive influence, quite similar to that which exists between the dissolved molecules (A), which makes itself felt between these molecules and the wall. The dissolved molecules are thus kept at a distance, and above all will not be allowed to enter any of the capillary canals of the wall. On the other hand, a molecule of water (B) which has already entered one of these capillaries is in equilibrium if

<sup>1</sup> The structure of the semipermeable membrane being quite unknown, the diagram only very vaguely represents its inner surface.

we only consider the attractions to which it is subjected by other molecules of water; there is, however, another force acting on this molecule, namely, the attraction of the nearest molecule A, and as this is not counterbalanced the molecule B is drawn towards the solution.

A continuous oozing of solvent through the wall towards the interior of the osmotic cell is thus established. The penetrating or entering water is at first attracted by the molecules A nearest the wall; it does not, however, remain with them but diffuses through the whole, for the equilibrium requires the equidistance of the dissolved molecules.

This is the qualitative interpretation of the phenomenon. It is not so easy to follow from the quantitative point of view, yet we may try to do so, starting with a theoretical deduction which we have already acquired. We have shown that in a solution the dissolved molecules tend to separate from each other up to what might be termed the gaseous distance, that is to say, the molecular attractions (or repulsions) tend towards a final effect whether it is a matter of dissolved or vaporised substance. If we could assume that equal active forces were required for these two modes of disintegration,<sup>1</sup> then the increase in volume of the same quantity of substance would in the two cases stop before the same obstacle. In other words, a pressure capable of limiting the expansion of the vaporised substance would suffice equally well to hinder (in osmotic pressure experiments) the increase in volume of the dissolved substance by the entrance of new molecules of solvent. We see at once that this conclusion is only another way of stating *van't Hoff's law*.

The molecular attraction, which we assume to explain even solution, suffices equally to interpret the phenomena of osmosis. Moreover, by taking this point of view we can

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<sup>1</sup> Supposing, of course, that the two processes could be carried out at the same temperature.

readily understand the relationship which exists between osmotic pressure, rise in boiling-point, and depression of freezing-point. By virtue of the preponderating attraction which exists between heterogeneous elements of a solution the dissolved substance attracts the solvent with a force which is equal to a certain osmotic pressure; it is, therefore, not astonishing to find that the dissolved substance utilises this force to prevent the solvent from separating from it by volatilisation, by freezing, or by any other process. The active cause being the same—the effects are correlative.

## FOURTH PART

## CHEMICAL MECHANICS

TOWARDS the end of last century the Swedish chemist *Bergmann* proposed a theory of the mode in which chemical forces act. In few words his doctrine was :—the chemical affinity of a substance manifests itself with an invariable intensity which may be expressed by a number. The reaction  $A C + B = A B + C$  goes on to completion, if the affinity of A is greater for B than it is for c.

The ideas promulgated by *Berthollet* in his '*Essai de statique chimique*' (1803) were quite different. According to him, the state of equilibrium resulting from a reaction depends first of all on the active masses of the substances, so that in a given system the determining action of each substance is proportional to the number of equivalents of it present.

If to a solution of one equivalent of sulphuric acid and one equivalent of nitric acid a solution of one equivalent of caustic soda were added, each of the acids would take up part of the base and each would be half neutralised. If the proportion of sulphuric acid were doubled, then after the addition of one equivalent of caustic soda there would be four-thirds of an equivalent of sulphuric acid and two-thirds of an equivalent of nitric acid still unsaturated.

*Berthollet* also foresaw that the normal division as determined by the active masses might be more or less modified under the influence of the state of condensation of the

matter. A complete or relative insolubility is favourable to the predominating formation of a substance. Thus the addition of sulphuric acid to a solution of barium chloride gives rise to the formation of the greatest possible quantity of barium sulphate. The division of the base between the acids takes place normally; but as the sulphate is precipitated it is withdrawn from the system and the equilibrium is disturbed. A renewal of the reaction takes place with formation of a fresh quantity of insoluble salt; and this goes on until either the sulphuric acid or the barium is completely precipitated.

In an analogous manner, when a volatile substance is formed the equilibrium only becomes stable after the complete elimination of the gaseous product.

The ideas of *Berthollet* were ingenious; they tended to liken the effects of affinity to those of gravitation, and to bring the laws regulating chemical actions within the sphere of mechanics.<sup>1</sup> These ideas can still be traced in modern works on chemistry, at least in the special cases relating to precipitation and gas evolution. In their general form, however, *Berthollet's* theories do not agree with observed facts.

In 1867 the Norwegian chemists *Guldberg and Waage* improved *Berthollet's* system by introducing a new factor. The intensity with which two substances tend to react with each other can be expressed by the product  $k p q$ ,  $p$  and  $q$  denoting the *active masses*, that is, *the number of equivalents by which the substances are represented in unit volume*, and  $k$  an *affinity coefficient*.

In order to understand more clearly what this coefficient means let us see under what conditions two sub-

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<sup>1</sup> In applying these theories of chemical combination *Berthollet* came to the conclusion that two elements might unite in any proportions whatever and thus form an infinite variety of substances. *Haknew*, for instance, quite a series of mercury oxides.—*Proust* contradicted him on this point, and the result of the extremely courteous discussion between the two scientists is our second law of chemical combination—the law of constant proportions.

stances  $AA'$  and  $BB'$  (elementary or compound)<sup>1</sup> can give rise by a double exchange to two new substances  $AB$  and  $A'B'$ .

The conditions are :

1. That the affinities or valencies of the atoms must be satisfied in the new compounds.

2. That the original molecules must be endowed with a sufficient mobility for them to come into close contact. This amounts to '*corpora non agunt nisi fluida*,' and a transposition is only possible if at least one of the reacting substances is liquid, dissolved, or gaseous.<sup>2</sup>

3. That the temperature be favourable to the reaction. Chemical reactions, even the most violent ones, do not take place except between certain temperature limits. Hydrogen and oxygen only combine with explosion above  $620^{\circ}\text{C}.$ ,<sup>3</sup> and hydrogen and chlorine likewise only unite under the influence of heat or of light.

Experiments performed by *Donny and Mareska* (1845) and by *Raoul Pictet* (1892-1893) show that at  $-80^{\circ}\text{C}.$  the most energetic reactions (at ordinary temperatures) with which we are acquainted do not take place at all: sulphuric acid has no action on barium chloride, hydrochloric acid none on silver nitrate, sulphuric acid none on sodium, and sodium none on alcohol. Towards  $-125^{\circ}\text{C}.$  chemical activity seems to be entirely suspended. And the reason of this inertness is not difficult to understand. Let us notice that in the substances brought together the

<sup>1</sup>  $A$  and  $A'$  or  $B$  and  $B'$  may be identical or different atoms.

<sup>2</sup> We are, however, acquainted with a few reactions between solids.

Barium sulphate and potassium carbonate (and inversely barium carbonate and potassium sulphate) enter into reaction without either of them being dissolved, it being only necessary to mix them together in a finely powdered state. Under the influence of a strong pressure (up to 6,000 atmospheres) the reaction is fairly energetic (*Spring*).

<sup>3</sup> A mixture of hydrogen and oxygen explodes when heated to  $620-680^{\circ}\text{C}.$  (*V. Meyer and Münch*).—Silent combination takes place slowly at  $300^{\circ}$ .—At  $100^{\circ}$  the reaction is so slow that it cannot be experimentally followed (*V. Meyer and Raun*).

atoms A and A' on the one hand, and B and B' on the other, attract each other *at atomic distance*, and that so intimate a union would not be easily broken down by external attractions acting at the comparatively great distances which separate the molecules. It is, therefore, probable that the *status quo* would be maintained indefinitely if it were only necessary to take into account the action of the affinities. But the kinetic theory teaches us that the material particles are not in a state of rest, but that the molecules move about, and that the atoms themselves vibrate around a position of equilibrium; and from this we may assume that the meeting of two heterogeneous molecules may be accompanied by certain circumstances which are favourable to the establishment of new unions. This would be so if the contact<sup>1</sup> of these molecules took place at the two atoms which are predisposed to unite, and at the moment when the oscillation phase of the atoms was greatest and the atoms were thus thrown towards the exterior of the molecules. Under these circumstances the extra-molecular attraction (of B for A, for example) would become preponderating and would bring about the double exchange. But if the possibility of a chemical reaction depends on the atomic and molecular movements, it must also depend *on the temperature*, for those movements are functions of this.

These explanations will suffice to show that the *coefficient k* is a constant which refers to the nature of the substances brought together, to the temperature, and to the other physical conditions of the reaction.

We have now to interpret the *rôle* of the *active masses*. If one gram-equivalent of each of the substances AA' and BB' be dissolved in 1 litre of solution, there will be a certain number of molecular collisions per second. Only collisions

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<sup>1</sup> The word *contact* must not be taken in a too literal sense. A more or less close approach of the two heterogeneous molecules is rather to be understood.



between heterogeneous molecules can give rise to a transposition of atoms. If now another gram-equivalent of  $BB'$  be dissolved in the solution (the concentration of  $BB'$  being thus doubled), then the molecules  $AA'$  will have twice the number of chances of colliding with  $BB'$  molecules, and the speed of the reaction will become  $1 \times 2$  times as great as before. If now the concentration of  $AA'$  be doubled, this will again double the number of collisions favourable to double exchange, and the speed of the reaction will become  $2 \times 2$  times greater than the initial speed. We see, therefore, *a priori* that this speed becomes proportional to the product of the active masses.

It is to be understood that the reaction commences with a speed which is determined by the masses of the substances brought together. But as the transposition goes on these masses diminish and the chemical phenomenon abates. We know several reactions the completion of which extends over a time sufficiently long to allow of an experimental study of their speeds.

Our study will now be divided into a *static* part, treating of chemical equilibrium; a *dynamic* part, relating to the speed of reactions; and a more general chapter, in which we shall again return to the theories of the constitution of salt solutions.

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## I. CHEMICAL EQUILIBRIUM

### A. REVERSIBLE REACTIONS

By the action of acetic acid on ethyl alcohol, ethyl acetate and water are produced. And, inversely, water tends to saponify the ester formed and reproduce the original substances. Both esterification and saponification are generally incomplete reactions which mutually limit each other and lead to a state of equilibrium determined by the equality of the speeds of the inverse transformations. We

know many reactions of this kind, and the equilibrium which they give rise to may be expressed by the equation :

$$k(a-x)(b-x)(c-x)\dots\dots = k_1(a_1+x)(b_1+x)(c_1+x)\dots\dots$$

This equation refers to substances A, B, C,.....  $A_1, B_1, C_1, \dots\dots$  which form two systems capable of being transformed into each other. The letters  $a, b, c, \dots\dots$   $a_1, b_1, c_1, \dots\dots$  denote the initial active masses, and  $k$  and  $k_1$  are the activity coefficients of the two opposite transformations. The equation tells us that a quantity  $x$  of the bodies of the first system has given rise to a corresponding quantity of substances of the second system, and that at this moment a stationary equilibrium has been established because the two opposite reactions have attained the same speed.

*Remarks.*—I. Only substances whose concentration is subject to variation exert a variable influence on the equilibrium or on the speed of a reaction ; gases and dissolved substances belong to this category.—Insoluble substances, on the contrary, have a particular density and an invariable concentration, and their influence must be expressed by a *constant active mass*.<sup>1</sup>

2. To determine the variable active masses it is necessary to apply rigorously the definition already given, i.e. to take account of the number of equivalents per unit of volume (per litre).

3. It frequently happens that the two sides of the equation of equilibrium contain the same number of factors  $(a-x)$ ,  $(b-x)$ , &c. In such cases it is sufficient to take

<sup>1</sup> This principle, stated in 1867 by *Guldberg and Waage*, may be accepted as an empirical rule.—Besides, an explanation has been given according to which the so-called insoluble substances are *not absolutely unable* to diffuse in water (or some other medium), but must rather be considered as endowed with an exceedingly small solubility. If this be true, and indeed it seems to be so, then in a mixed system the concentration, or active mass, of such a substance will be *constant* (i.e. as great as possible), provided the temperature be constant and a residual quantity of the substance be left undissolved.

account of the number of equivalents of each substance in the medium in which the reaction is taking place. The volume of this medium does not then influence the values of the constants  $k$  and  $k_1$ .

FIRST EXAMPLE. EQUILIBRIUM OF ESTERIFICATION AND OF SAPONIFICATION.—When we bring together  $a$  equivalents of acetic acid,  $b$  of alcohol,  $a_1$  of ethyl acetate, and  $b_1$  of water, stationary equilibrium is established after a few hours if the operation be performed at  $100^\circ\text{C}$ . (or after a few days if it take place at the ordinary temperature). A simple titration tells us then what quantity of acetic acid is still free, and from this we can calculate the active masses of the other three substances.

From the equation of equilibrium :

$$k(a-x)(b-x) = k_1(a_1+x)(b_1+x)$$

we find :

$$\frac{k}{k_1} = \frac{(a_1+x)(b_1+x)}{(a-x)(b-x)}.$$

In order to find the value of the ratio  $\frac{k}{k_1}$  we first take the simplest case, in which  $a=b=1$  and  $a_1=b_1=0$ . The equation then becomes :

$$k(1-x)^2 = k_1 x^2,$$

and

$$\frac{k}{k_1} = \frac{x^2}{(1-x)^2}.$$

Now, when we allow one equivalent of acetic acid to act on one of alcohol, esterification takes place to the extent of 66 per cent. The value of  $x$  is therefore 0.66, and

$$\frac{k}{k_1} = 4.$$

If *Guldberg and Waage's* theory is true, this ratio must be constant. We can, therefore, calculate what the value of  $x$  (the degree of esterification) will be if the initial quantities ( $a, b, a_1, b_1$ ) of the substances be varied. The

results obtained by *Berthelot and Péan de Saint-Gilles* are given in the following table :

Substances employed				Value of $x$	
Acid ( $a$ )	Alcohol ( $b$ )	Ester ( $a_1$ )	Water ( $b_1$ )	Calculated	Observed
1	1	—	—	—	0.665
1	2	—	—	0.845	0.828
2	1	—	—	0.845	0.858
1	1	—	3	0.409	0.407
1	2	—	98	0.073	0.073
1	4	—	—	0.930	0.902
1	1	1.6	—	0.492	0.521

Experiment and theory do not *absolutely* agree, still the agreement is quite sufficient.

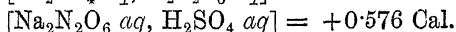
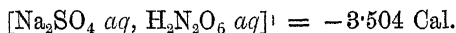
SECOND EXAMPLE. ACTION OF AN ACID ON A SALT IN AQUEOUS SOLUTION.—As we consider here reactions in which no precipitation occurs, the division of the base between the two acids could not be determined by chemical analysis. But physical chemistry teaches us several methods of investigating the problem, and we shall here consider the two principal ones.

*a. Study of the thermal effect of the reaction (in dilute aqueous solution).<sup>1</sup>*

In speaking of neutralisation phenomena, we have omitted to mention an indirect method of determining the difference of the heats of neutralisation of two salts. When an equivalent of sodium sulphate ( $\frac{1}{2}$  gram-molecule) reacts on an equivalent of nitric acid (1 gram-molecule), a certain thermal effect is produced. Quite a different thermal effect results from the action of an equivalent of sulphuric acid on an equivalent of sodium nitrate. The final equilibrium is the same in both cases ; the difference in the observed effects

<sup>1</sup> In order to give an account of this work of *Thomsen's* we shall take up the old view of the constitution of salt solutions, and in the meantime let us forget the theories discussed at the end of the third part of the book.

must, therefore, correspond to the difference of the initial states, that is, to the complete displacement of one acid by the other. *Thomsen* has found that



By the displacement of the sulphuric acid by the nitric acid, therefore, 4.080 Cal. are absorbed, that is, 2.040 Cal. per equivalent. The difference of the heats of neutralisation directly determined for an equivalent of sulphate and an equivalent of nitrate of sodium is 2.072 Cal.

Let us recall that the action of an acid on a salt of the same acid often gives a considerable thermal effect. We know also by the law of thermoneutrality that on mixing two neutral salt solutions generally no appreciable effect is produced; and we may further add that the same remark applies to two dilute solutions of different acids.

We can now approach the main point of the subject and show how thermo-chemistry gives us a solution of the problem under discussion.

If we allow a dilute solution of one equivalent of nitric acid (*a*) to react on a dilute solution of one equivalent of sodium sulphate (*b*), stationary equilibrium will be established when a quantity *x* of the acid has reacted on the salt to form free sulphuric acid (*a*<sub>1</sub>) and sodium nitrate (*b*<sub>1</sub>). We then have as before:

$$k(1-x)^2 = k_1x^2,$$

and

$$\frac{k}{k_1} = \frac{x^2}{(1-x)^2}.$$

The observed thermal effect will be due to two distinct causes:

1. The transformation of *x* sulphate into *x* nitrate;
2. The action of *x* free sulphuric acid on the remaining (1 - *x*) sulphate.<sup>1</sup>

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<sup>1</sup> *x* is a fractional number.

From the thermo-chemical point of view all the other actions can be neglected.

The effect due to the *first* cause would be  $x$  times the difference between the heats of neutralisation of sodium nitrate and of sodium sulphate, that is,  $-2.072x$ .

The value of the effect due to the *second* cause would be the same as  $(1-x)$  times the effect produced by the action of  $\frac{x}{1-x}$  sulphuric acid on 1 of sodium sulphate.

Now, *Thomsen* has found that

$$\left[n \frac{1}{2} \text{H}_2\text{SO}_4 \text{ aq}, \frac{1}{2} \text{Na}_2\text{SO}_4 \text{ aq}\right] = -\frac{n}{n+0.8} 1.65 \text{ Cal.}$$

From this we deduce :

$$\begin{aligned} (1-x) \left[ \frac{x}{1-x} \cdot \frac{\text{H}_2\text{SO}_4}{2} \text{ aq}, \frac{\text{Na}_2\text{SO}_4}{2} \text{ aq} \right] \\ = - (1-x) \frac{\frac{x}{1-x}}{\frac{x}{1-x} + 0.8} 1.65 \text{ Cal.} \end{aligned}$$

The result of the calorimetric determination of this reaction is an absorption of 1.752 Cal., so that we can write

$$x(-2.072) - (1-x) \frac{\frac{x}{1-x}}{\frac{x}{1-x} + 0.8} 1.65 = -1.752.$$

The solution of this equation gives for the value of  $x$  0.665, from which we deduce

$$\frac{k}{k_1} = 4.$$

If now the reacting products be mixed in other pro-

portions, this ratio remains constant, and by means of it the value of  $x$  can be calculated from the equation

$$k(a-x)(b-x) = k_1(a_1+x)(b_1+x).$$

Knowing thus the division of the base between the acids we can calculate the accompanying thermal effect and confirm theory by experiment. *Thomsen* has found :

Equivalents mixed				Thermal effect	
(a)	(b)	(a <sub>1</sub> )	(b <sub>1</sub> )	Calculated	Observed
$\frac{1}{2}$	1	—	—	-1.331 Cal.	-1.292 Cal.
1	1	—	—	-1.773 „	-1.752 „
2	1	—	—	-1.974 „	-2.026 „
2	1	1	—	-0.982 „	-0.978 „
—	—	1	1	+0.298 „	+0.288 „
—	—	2	1	+0.348 „	+0.379 „

There is no doubt about the conclusion—*Guldberg and Waage's* theory is in this case also supported by facts.

If we return now to the simplest case

$$(a = b = 1, a_1 = b_1 = 0),$$

we see that

$$\sqrt{\frac{k}{k_1}} = \frac{x}{1-x} = 2.$$

The ratio  $\frac{x}{1-x}$  tells us how many times  $x$  (the quantity of nitric acid which is transformed to nitrate) is greater than  $1-x$  (the quantity of remaining sulphate). This ratio is termed the *avidity*, and expresses, according to *Thomsen*, the relative energy with which the acids tend to seize their part of the base.<sup>1</sup> The following table gives the relative avidity for a number of acids compared with nitric acid as standard :—

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<sup>1</sup> The equation of equilibrium contains the active mass of the acid and also that of the base; that is the reason why the ratio  $\frac{k}{k_1}$  is equal to the square of the avidity. This is confirmed by other functions which we shall study later.

Acids	Avidity	Heat of neutralisation by NaOH
$\text{HNO}_3$ . . . .	1.00	13.68 Cal.
$\text{HCl}$ . . . .	1.00	13.74 „
$\text{HBr}$ . . . .	0.89	13.75 „
$\text{HI}$ . . . .	0.79	13.68 „
$\frac{1}{2}\text{H}_2\text{SO}_4$ . . . .	0.49	15.69 „
$\frac{1}{2}\text{H}_2\text{SeO}_4$ . . . .	0.45	15.19 „
$\text{H}_3\text{PO}_4^*$ . . . .	0.13	14.80 „
$\frac{1}{2}\text{C}_2\text{H}_2\text{O}_4$ . . . .	0.24	14.14 „
$\text{CH}_3\text{Cl.CO}_2\text{H}$ . . . .	0.09	14.28 „
$\text{HF}$ . . . .	0.05	16.27 „
$\frac{1}{2}$ Tartaric acid . . . .	0.05	12.65 „
$\frac{1}{3}$ Citric acid . . . .	0.05	13.00 „
$\text{CH}_3\text{CO}_2\text{H}$ . . . .	0.03	13.40 „
$\text{HCN}$ . . . .	0.00	2.77 „

As can be seen, the avidities are not at all proportional to the heats of neutralisation. So that the heat of neutralisation cannot be considered as a measure of the affinity of an acid for a base.

For bases formed from the divalent metals (Mg, Mn, Fe, Zn, Co, Ni, Cu) *Thomsen* has found that the relative avidity of sulphuric acid varies between 0.7 and 0.81, nitric acid being taken as standard of comparison. Similar irregularities have been noticed for the other polybasic acids.

*β. Study of the change of volume which accompanies the reaction.*

*Ostwald's* method is to dissolve one gram-equivalent of a base or of an acid in a quantity of water, such that the total weight of the solution is 1 kilogram. The density of the solution is then determined by means of a pycnometer, and from this the volume (at 20°C.) is deduced.

By neutralising one equivalent of base by one equivalent of acid, a salt solution is obtained which weighs 2 kilograms. A determination of the density of this solution with the pycnometer, and calculation of its volume, shows that this volume is not equal to the sum of the

\* For the first equivalent of soda.



volumes mixed, but that an expansion or a contraction of a certain number of cubic centimetres has taken place.

The difference between the volume changes which accompany the neutralisation of the same acid by two different bases is practically constant whatever be the acid. The expansion caused by neutralisation with caustic potash is on the average 0.21 c.c. greater than that caused with caustic soda, and 25.97 c.c. greater than that when ammonia is used (in this last case the effect is negative, that is, a contraction takes place).

The following table gives some results for the expansion by neutralisation :

Acids	Expansion in cubic centimetres produced by neutralisation with		
	KOH	NaOH	NH <sub>3</sub>
HNO <sub>3</sub> . . . .	20.05	19.77	- 6.44
HCl . . . . .	19.52	19.24	- 6.57
CCl <sub>3</sub> .CO <sub>2</sub> H . . .	17.36	17.07	- 8.66
CHCl <sub>2</sub> .CO <sub>2</sub> H . . .	12.95	12.70	-12.97
CH <sub>2</sub> Cl.CO <sub>2</sub> H . . .	10.85	10.63	-15.09
CH <sub>3</sub> .CO <sub>2</sub> H . . . .	9.52	9.29	-16.26
Butyric acid . . .	6.96	6.84	-18.63
Isobutyric acid . .	6.30	6.17	-19.27
Average difference	0.21	25.76	

The following table shows by how much the expansion which accompanies neutralisation of different acids is greater than that of isobutyric acid (the smallest expansion yet found). We see that the differences are almost independent of the nature of the base used.

	By KOH	By NaOH	By NH <sub>3</sub>	Mean
HNO <sub>3</sub> . . . . .	13.75	13.60	12.83	13.39
HCl . . . . .	13.22	13.07	12.70	13.00
CCl <sub>3</sub> .CO <sub>2</sub> H . . .	11.06	10.89	10.60	10.85
CHCl <sub>2</sub> .CO <sub>2</sub> H . . .	6.65	6.53	6.30	6.49
CH <sub>2</sub> Cl.CO <sub>2</sub> H . . .	4.55	4.45	4.18	4.39
CH <sub>3</sub> .CO <sub>2</sub> H . . . .	3.22	3.11	3.01	3.11
Butyric acid . . .	0.68	0.67	0.64	0.66

By the aid of the mean differences found we can calculate theoretically the change of volume which must correspond to the neutralisation of a certain base by a certain acid.

We know that for ammonium isobutyrate the expansion is  $-19.27$ . Denoting by  $a$  and  $b$  the respective influences of the acid and of the base, we may write  $a + b = -19.27$ . If instead of isobutyric acid another acid be taken, then instead of  $a$  we shall have the following values:  $a + 0.66$  for butyric acid,  $a + 3.11$  for acetic acid, and so on up to  $a + 13.39$  for nitric acid.

If we take another base instead of ammonia, we shall have the following expansions:

$$\text{For KOH: } b + 25.97 = -a - 19.27 + 25.97 = -a + 6.70$$

$$\text{For NaOH: } b + 25.76 = -a - 19.27 + 25.76 = -a + 6.49$$

To calculate now the change of volume which would take place by the neutralisation, for example, of monochloroacetic acid by caustic soda, we find:

$$(a + 4.39) + (-a + 6.49) = 10.88 \text{ (instead of } 10.63).$$

(for the acid)                      (for the base)

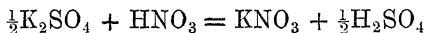
The factor  $a$ , the value of which is unknown, is, therefore, eliminated; and we clearly see that *the change of volume which accompanies neutralisation is additively composed of two factors, one of which depends only on the nature of the acid, and the other only on the nature of the base*. This recalls to us the law of thermo-neutrality, as well as the ratio of the electric conductivities of solutions.

Suppose now that we mix together three solutions (prepared as above directed), one containing an equivalent of hydrochloric acid, one an equivalent of caustic potash, and the third an equivalent of ammonia. The change of volume will depend on how much potash and how much ammonia seize the acid, and from the observed expansion the division of the acid between the two bases can be deduced.

Having now given the principle on which this new method of investigation is based, we shall return to the reaction which has already been studied from the thermo-chemical<sup>1</sup> point of view—namely, the action of  $\frac{1}{2}\text{K}_2\text{SO}_4$  on  $\text{HNO}_3$ .

One gram-equivalent of potassium sulphate is dissolved in so much water that the solution weighs 2 kilograms. One gram-equivalent of nitric acid is contained in 1 kilogram of solution.

If the reaction



were to take place completely, there would be an expansion of 8.17 c.c. By the pycnometer we ascertain that a solution of

$\frac{1}{2}\text{K}_2\text{SO}_4$	has a volume of	1,931.75 c.c.
$\text{HNO}_3$	„ „ „	966.60 „
$\text{KNO}_3$	„ „ „	1,938.11 „
$\frac{1}{2}\text{H}_2\text{SO}_4$	„ „ „	968.41 „

The sum of the first two volumes is less by 8.17 c.c. than the sum of the last two.

But certain *secondary reactions* must be taken into account.

Between the two salts and between the two acids no volume reactions take place. For the action nitrate + nitric acid it is negligible; but the action of sulphuric acid on the sulphate is quite considerable. *Ostwald* gives:

$\frac{1}{2}\text{K}_2\text{SO}_4 + \frac{1}{2}\text{H}_2\text{SO}_4$	:	expansion =	3.545 c.c.
$\frac{1}{2}\text{K}_2\text{SO}_4 + \text{H}_2\text{SO}_4$	:	„	= 4.625 „
$\frac{1}{2}\text{K}_2\text{SO}_4 + 2\text{H}_2\text{SO}_4$	:	„	= 4.900 „

From these data the volume change which accompanies the establishment of a certain state of equilibrium can be calculated. Suppose that in the reaction under examina-

<sup>1</sup> *Thomsen* has shown by a thermo-chemical method that for the alkalis (not only for  $\text{NaOH}$ , but also for  $\text{KOH}$ , and  $\text{NH}_3$ ) the avidity of nitric acid and that of sulphuric acid are in the ratio 2 : 1.

tion a quantity  $x$  of the nitric acid ( $a$ ) decomposes a corresponding quantity of the sulphate ( $b$ ) setting sulphuric acid ( $a_1$ ) free. We shall then have in solution

$$(1 - x)b + (1 - x)a + xb_1 + xa_1.$$

The change in volume will be equal to  $x$  times the expansion which would take place if the reaction were a complete one, plus the effect produced by the free sulphuric acid on the remaining sulphate. If we put this in algebraic form we get

$$x \times 8.17 + [xa_1 \times (1 - x)b].$$

If we accept the conclusion which we deduced from the thermo-chemical study—namely, that the reaction takes place to the extent of 66 per cent. or two-thirds—then the expansion which should be observed is

$$\frac{2}{3} \times 8.17 + \frac{1}{3} \times 4.625 = 7 \text{ cubic centimetres.}$$

This calculated result has been experimentally confirmed so that *the two methods of investigation, the thermo-chemical and the volumetric, indicate the same division of the base between the two acids.*

By this volumetric method *Ostwald* determined the relative *avidity* of nitric acid, hydrochloric acid, and sulphuric acid with reference to different bases.

Bases	Avidity ratio		
	$\frac{\text{HNO}_3}{\frac{1}{2}\text{H}_2\text{SO}_4}$	$\frac{\text{HCl}}{\frac{1}{2}\text{H}_2\text{SO}_4}$	$\frac{\text{HCl}}{\text{HNO}_3}$
KOH	2.00	1.94	0.97
NaOH	2.00	1.92	0.96
NH <sub>3</sub>	1.88	1.81	0.96
$\frac{1}{2}\text{MgO}$	1.76	1.74	0.99
$\frac{1}{2}\text{ZnO}$	1.61	1.53	0.95
$\frac{1}{2}\text{CuO}$	1.44	1.40	0.97

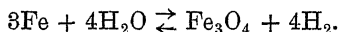
The avidity ratio  $\frac{\text{HCl}}{\text{HNO}_3}$  is constant for all bases.

Sulphuric acid behaves somewhat irregularly,—its avidity being greater when referred to Mg, Zn, Cu, and

the other divalent metals, than for the monovalent. The reason of this must be traced to the acid sulphates, which are more or less readily formed according to the nature of the base. But it will be sufficient to have called attention to this point. The following are some acids to which *Ostwald* has applied his method, along with the results he obtained :

	Avidity		Avidity
HNO <sub>3</sub> . . . .	1.00	CH <sub>2</sub> OH.CO <sub>2</sub> H . .	0.05
HCl . . . . .	0.98	CH <sub>3</sub> .CO <sub>2</sub> H . . .	0.0123
CCl <sub>3</sub> .CO <sub>2</sub> H . . .	0.80	Butyric acid . . .	0.0098
CHCl <sub>2</sub> .CO <sub>2</sub> H . .	0.33	Isobutyric acid . .	0.0092
CH <sub>2</sub> Cl.CO <sub>2</sub> H . . .	0.07		

These examples might be multiplied, and it might be shown that certain other physical properties, particularly those which are in direct correlation with the density,<sup>1</sup> may be used to reveal the nature of the equilibrium in more or less complex solutions. These, however, will not be gone into, but just before closing this chapter I should like to say a word or two about a very interesting reaction in which the substances exert an influence BY CONSTANT ACTIVE MASSES. The work of *Deville* (1871) on the action of steam on metallic iron and of hydrogen on ferroso-ferric oxide is well known. These two actions which take place at a high temperature are reversible :



The stationary equilibrium does not in any way depend on the relative quantities of iron and of the magnetic oxide, but only on the presence of these substances and on the proportion of hydrogen mixed with the water-vapour. This proportion may be so much the smaller as

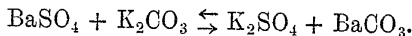
<sup>1</sup> More particularly the refractive power and the power of absorbing light. By a study of the rotation *Jellet* has been able to determine the distribution or division of hydrochloric acid between two alkaloids in alcoholic solution: the alkaloids studied were quinine, codeine, and brucine.

the temperature is higher, that is to say, a lower proportion will counterbalance the action of the vapour if the temperature is higher. These facts are expressed in the equation

$$k \pi (a - x) = k_1 \pi_1 (a_1 + x),$$

in which  $\pi$  and  $\pi_1$  are the constant active masses,  $a$  and  $a_1$  the initial masses of the gaseous products.

A similar example has been studied by *Guldberg and Waage*—namely, the reversible reaction



As the theory predicts, it has been found that the equilibrium requires a constant ratio (1 : 1) between the active masses of the soluble substances  $\text{K}_2\text{CO}_3$  and  $\text{K}_2\text{SO}_4$ .

(See also *Nernst*, 'Theoretische Chemie,' 1898, p. 498.)

## B. DISSOCIATION PHENOMENA

When a substance is decomposed by heat, giving one or more volatile products, similar equilibria are observed to those which obtain in the case of reversible reactions.

*Calcium carbonate*, for example, commences to decompose about 450°C. into lime and carbon dioxide. To each degree of temperature there corresponds a dissociation pressure, that is, a certain concentration of the gaseous product. According to *Guldberg and Waage's* theory, equilibrium will be established when

$$k \pi = k_1 \pi_1 u.$$

In this equation  $k$  and  $k_1$  have their usual signification (and are functions of the temperature),  $\pi$  and  $\pi_1$  denote the constant active masses of the undecomposed carbonate and of the lime formed, and  $u$  is the variable concentration (pressure) of the evolved carbon dioxide. The only

variable,  $u$ , must attain a certain value, which will depend on  $k$  and  $k_1$ , and consequently on the temperature. If, by means of an external pressure, the volume of the carbon dioxide be decreased, the concentration of the gas will be increased, and in order that equilibrium may be re-established a certain quantity of  $\text{CaO}$  and  $\text{CO}_2$  will recombine.<sup>1</sup>

In an analogous manner, salts which contain molecules of water of crystallisation exhibit a vapour tension which is solely governed by the temperature. Sodium phosphate ( $\text{Na}_2\text{HPO}_4 \cdot 12\text{aq}$ ) is an example of this class: at a certain temperature its vapour tension remains constant as long as *all* the salt has not been transformed into  $\text{Na}_2\text{HPO}_4 \cdot 7\text{aq}$ . After this limit has been attained, the vapour tension diminishes, because then it is a different substance which is dissociating.

When, by the dissociation of a solid body, *two* volatile products are formed, the equation of equilibrium is

$$k\pi = k_1 u_1 u_2,$$

and it tells us that the *product* of the variable concentrations (partial pressures) must rise to a certain value, equal to  $\frac{k\pi}{k_1}$ , and dependent on the temperature. This is the case for *ammonium hydrosulphide*  $\text{NH}_4\text{HS}$ , which is

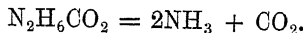
<sup>1</sup> Instead of relying on the *empirical constant active mass rule*, we may assume (as Nernst does in *Dammer's 'Handbuch,'* i. 251) that the so-called non-volatile substances are, in reality, endowed with a certain very small tension of sublimation. In the gaseous system produced by the dissociation of calcium carbonate, the  $\text{CaCO}_3$  and  $\text{CaO}$  molecules will then be represented by the very small active masses  $\pi$  and  $\pi_1$ , and these will depend only on the temperature (and not at all on the quantities of the residual solid substances).

The concentration of the carbon dioxide will be  $u = \frac{k\pi}{k_1\pi_1}$ , and determined only by the temperature. As  $\pi$  and  $\pi_1$  are supposed to be very small, the pressure of the carbon dioxide gas will scarcely be different from that of the whole system. The reader will easily find a similar interpretation for some other examples of dissociation referred to in this chapter.

dissociated into equal volumes of hydrogen sulphide and ammonia. At  $25.1^{\circ}\text{C}$ ., the dissociation pressure of this substance is equal to 50.1 centimetres of mercury: this corresponds to a partial pressure of 25.05 cm. for each of the constituents.

If the dissociation takes place in an atmosphere of hydrogen sulphide at a pressure of 8.6 cm., the dissociation-pressure attains the value 50.4 cm.—there is an increase of 41.8 cm.; the partial pressure due to the ammonia is equal to half the increase, viz. 20.9 cm., and that due to the hydrogen sulphide is the other half of the increase plus the original pressure,  $20.9 + 8.6 = 29.5$  cm. In agreement with theory, the products of the partial pressures ( $25.05 \times 25.05$  in the first case, and  $29.5 \times 20.9$  in the second) have the same value. Various experiments performed by *Isambert* confirm the equation of equilibrium.<sup>1</sup>

*Ammonium carbamate*, on heating, is decomposed as follows:



The equation of equilibrium in this case<sup>2</sup> is

$$k\pi = k_1 u_1^2 u_2,$$

and it tells us that at a given temperature the product of the variable concentrations (partial pressures) has a constant value.

All the preceding examples relate to the dissociation of solid substances. Even ammonium hydrosulphide and ammonium carbamate may be considered as passing directly from the solid to the dissociated state, because their vapour contains only a negligible proportion of undecomposed molecules.

<sup>1</sup> From this we see that the initial presence of one of the products of decomposition offers a resistance to the dissociation.

<sup>2</sup> As two molecules of ammonia take part in the reaction, it figures in the equation of equilibrium as the square of the active mass.



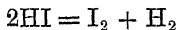
When the original substance itself is a gas or a vapour, one more variable must be taken into consideration, and the equation becomes

$$ku = k_1 u_1 u_2,$$

and requires that at a certain temperature the ratio  $\frac{u_1 u_2}{u}$  has a constant value. Examples of this case are *phosphorus pentachloride, ammonium chloride, amylene hydrochloride, nitrogen peroxide, &c.*<sup>1</sup> For all these substances the dissociation is accompanied by an increase in volume, and *the equilibrium is influenced by the pressure.*

Suppose that by increasing the external pressure we reduce the gaseous products to a fraction of their original volume: the concentrations  $u$ ,  $u_1$ , and  $u_2$  will increase in the same proportion, the ratio  $\frac{u_1 u_2}{u}$  will no longer have its equilibrium value, and some of the dissociated products will recombine.

The case of hydriodic acid (studied by *Lemoine*) is very different. For the dissociation



we have the equation

$$ku^2 = k_1 u_1 u_2.$$

A constant value of the ratio  $\frac{u_1 u_2}{u^2}$  corresponds to each temperature. But as the decomposition does not alter the number of molecules, the degree of dissociation is quite independent of the pressure. The phenomenon represents a simple reversible reaction rather than a true case of dissociation.

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<sup>1</sup> The dissociation of  $\text{PCl}_5$ ,  $\text{NH}_4\text{Cl}$ , and  $\text{C}_5\text{H}_{11}\text{Cl}$ , has been studied by determining their vapour densities at fairly high temperatures. In these experiments it is evident that no part of the substance was left unvaporised.

## II. CHEMICAL DYNAMICS

## STUDY OF THE SPEED OF REACTION

WE know numerous reactions which take place sufficiently slowly to allow of the progress of the transformation being experimentally determined. Let us take as an example the decomposition of saccharose into dextrose and fructose (lævulose) by means of dilute acid. This transformation is not reversible. The acid acts by a so-called catalytic influence, and its original concentration is not altered during the course of the reaction. The only variable mass which has to be considered is that of the sugar,<sup>1</sup> and this concentration can easily be ascertained by polarimetric analysis. As this concentration diminishes as the decomposition progresses, the speed of the reaction continually decreases.

If the initial quantity of the sugar dissolved is  $a$ , then after a time  $t$  there is only a residual quantity  $(a-x)$  left undecomposed. If now the experiment be extended over a very short time  $dt$ , a further quantity of sugar  $dx$  will be transformed, and consequently the speed of the reaction is  $\frac{dx}{dt}$  at the moment  $t$ . But we can also express this speed in another way: for unit weight of sugar dissolved<sup>2</sup> it would be  $\kappa$ , for the quantity  $(a-x)$  it is  $\kappa(a-x)$ . We therefore have the equation<sup>3</sup>

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<sup>1</sup> The products of decomposition need not be taken into account since the reaction is not reversible.

<sup>2</sup> As the chemical reaction in question is uni-molecular, we may express the quantity of sugar either by units of weight (grams in solution) or by the active mass (number of equivalents per litre). In the equation of pluri-molecular reactions, which we shall meet with later, only the *active masses* or concentrations may be used.

<sup>3</sup> The integral calculus is here indispensable.

The constant  $\kappa$  has a special value which requires a word of explanation. It refers to the catalytic action of the acid employed,

$$\frac{dx}{dt} = k(a-x)$$

$$dt = \frac{1}{k} \cdot \frac{dx}{a-x}$$

and by integration,

$$t = \frac{1}{k} \ln \frac{1}{a-x} + c.$$

At the time 0, that is to say at the beginning of the reaction, the value of  $x$  is 0, and consequently

$$0 = \frac{1}{k} \ln \frac{1}{a} + c.$$

From these two last equations we find:<sup>1</sup>

$$t = \frac{1}{k} \ln \frac{a}{a-x}$$

$$k = \frac{1}{t} \ln \frac{a}{a-x} \quad (\text{equation 1}).$$

As the study of the speed of reactions is of great theoretical interest, and as no very special apparatus is required for the work, it may be desirable to give here some idea of

and is composed of two factors: the *speed-coefficient*  $k$  and the concentration of the acid. In reality, therefore,

$$k = kc.$$

<sup>1</sup> The constant  $c$  is often eliminated in another way. Two polarimetric tests are made, one at the time  $t$ , and the other at the time  $t_1$ , and from the equations

$$t = \frac{1}{k} \ln \frac{1}{a-x} + c.$$

$$t_1 = \frac{1}{k} \ln \frac{1}{a-x_1} + c.$$

we find

$$k = \frac{1}{t_1 - t} \ln \frac{a-x}{a-x_1} \quad (\text{equation 2}).$$

According to theory, the value of  $k$  must be constant. By experimentally determining the values  $x, x_1, x_2, \dots$  which correspond to the times  $t, t_1, t_2, \dots$  we can prove that this really is the case.

the *modus operandi*. This can best be done by the following two examples.

1. INVERSION OF CANE SUGAR.—According to *Ostwald*, the following procedure may be adopted: 10 cubic centimetres of sugar solution (200 grams per litre) are mixed with 10 cubic centimetres of normal hydrochloric acid solution in a small 20 c.c. flask which is kept in a bath (furnished with a thermostat) at 25°C. Before mixing, the liquids must be at the temperature 25°C., and this temperature must be carefully maintained during the whole course of the experiment. From time to time determinations of the rotation of the solution are made, and the *number of minutes* from the commencement of the experiment until each determination is made is noted. The polarimetric tube must, of course, be kept at 25°C., and after each determination of the rotation the solution should be put back into the small flask. Ten or more observations at convenient intervals of time<sup>1</sup> should be made, then, after an interval ten times longer than that required for the inversion of half of the sugar, the angle of rotation is determined for the last time. We may then calculate for each value of  $t$  the corresponding value of  $x$  (decomposed sugar), and make use of equation 2 to study the constancy of the coefficient  $\kappa$ . Or we may calculate directly from the rotations observed. In the equation

$$\kappa = \frac{1}{t_n} \cdot \log \frac{a_o - A}{a_n - A},$$

$a_o$  is the initial angle of rotation,  $a_n$  the angle observed at the time  $t_n$ , and  $A$  the final angle. This formula is only a modification of equation 1 and is based on this consideration—namely, that the initial quantity of sugar ( $a$  in equation 1) is proportional to the difference between the initial and the final rotations, exactly as the quantity

\* <sup>1</sup> The first observation is made immediately after starting the reaction; the following observations after intervals of 30 minutes, 60 minutes, 120 minutes, and so on.

$(a - x)$  of sugar remaining at the time  $t_n$  is proportional to the difference between the rotations  $a_n$  and  $A$ .

The result of this experiment is to give the value 0.00205 for  $k$ , if we use decimal logarithms (instead of natural logarithms as indicated in equation 1).

2. CATALYTIC ACTION OF DILUTE ACIDS ON METHYL ACETATE.—The experiment is carried out at 25°C. in a small flask which contains for 20 cubic centimetres of semi-normal acid (hydrochloric, sulphuric, &c.) 1 cubic centimetre of methyl acetate. The first acidimetric titration, for which 1 cubic centimetre of mixture is used, is made immediately after the reaction is started. After continuously increasing intervals, small quantities are drawn off and titrated; but the last 5 cubic centimetres must be left in the digester for at least two days, and these are used for the final determination. Denoting by  $a_0$ , the first titre (the number of cubic centimetres of  $\frac{1}{20}$ -normal baryta-water equivalent to 1 cubic centimetre of the acid mixture), by  $a, a_m, a_n, \dots$  the successive titres corresponding to the intervals of time  $t, t_m, t_n, \dots$ , and by  $A$  the final titre after the interval  $T$ , we have the equation

$$k = \frac{1}{t_n} \cdot \log \frac{A - a_0}{A - a_n}.$$

This formula is only a modification of equation 1, and is easily understood. For the operation described and for hydrochloric acid the value 0.0013 has been found for  $k$  (using decimal logarithms).

THE EQUATING OF PROBLEMS RELATING TO THE SPEED OF REACTIONS.<sup>1</sup>—The examples cited have been chosen from amongst the simplest cases, and now we must treat the question from a more general point of view. We must distinguish between reactions which go on to comple-

<sup>1</sup> The procedure given here is the classic one. For a simpler method of equation see *Th. Müller, Bulletin de la Société chimique de Paris*, [3], 19, p. 337. N.B.—It is necessary to rigorously apply the definition of active mass.

tion in a certain sense, and those which are reversible. For the first, the general type of equation will evidently be :

$$\frac{dx}{dt} = k(a-x)(b-x)(c-x).....$$

For the second, the momentary course of the reaction is the result of the difference in the speeds of the two reverse actions, so that

$$\frac{dx}{dt} = k(a-x)(b-x)(c-x) - k_1(a_1+x)(b_1+x)(c_1+x),$$

$a, b, c$ ;  $a_1, b_1$ , and  $c_1$  denoting as before the initial masses of the substances which constitute the two opposite systems.

The integration of these equations is always possible; moreover, it is generally simplified by the choice of the initial masses. Thus in order to apply the calculus to the experimental results obtained by *Berthelot and Péan de Saint-Gilles* (acetic acid and alcohol), *Guldberg and Waage* took up the simplified case in which  $a = b = 1$  and  $a_1 = b_1 = 0$ . The speed equation then becomes

$$\frac{dx}{dt} = k(1-x)^2 - k_1x^2.$$

The constants  $k$  and  $k_1$  are in the same ratio here as in the equation of equilibrium already studied.<sup>1</sup>

#### AVIDITY AND SPEED COEFFICIENT

To complete the study of the equilibria and speeds of reaction we must examine in how far these two methods of investigation lead to concordant results. Tables, drawn up by *Thomsen* and *Ostwald*, have already been given, showing the relative avidity of acids. Let us now see if the different acids, in such catalytic transformations as those mentioned above, exert an influence proportional to

<sup>1</sup> The transformation of  $\gamma$ -oxybutyric acid into water and lactone (and also inversely) is another example of the same kind (*P. Henry*).

their *avidity*. The table given below contains the principal results obtained in the SAPONIFICATION OF METHYL ACETATE and in the INVERSION OF CANE SUGAR.

The *catalysis of the acetate* was carried out as described above, but at the temperature  $26^{\circ}$  and at a different concentration (10 cubic centimetres of normal acid, 1 cubic centimetre of methyl acetate, and sufficient water to bring the volume up to 15 cubic centimetres). Column I. contains the coefficient  $\kappa$  for each acid, that is, the constant

$$\frac{1}{t_n} \cdot \log \frac{A - a_o}{A - a_n}.$$

In column II. the coefficients of speed, relative to that of hydrochloric acid taken as unity, are given. Column III. contains the constants  $\kappa$  deduced from the *rapidity of the inversion of the sugar*:

$$\left( \kappa = \frac{1}{t_n} \cdot \log \frac{a_o - A}{a_n - A} \right),$$

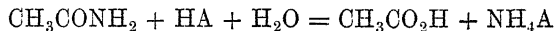
and in column IV. these constants are compared with that for hydrochloric acid. The figures of column V. are the relative avidities of the acids, according to *Thomsen* and *Ostwald*.

Acids	I.	II.	III	IV.	V.
Hydrochloric .	0.002412	1	0.002187	1	1
Hydrobromic .	2370	0.98	2438	1.114	0.89
Hydriodic .	2333	0.96			
Nitric .	2206	0.91	2187	1	1
Chloric .	2278	0.94	2261	1.035	
Sulphuric .	1319	0.55	1172	0.536	0.49
Ethylsulphuric .	2380	0.99	2186	1	
Ethylsulphonic .	2361	0.98	1993	0.912	
Benzenesulphonic	2394	0.99	2282	1.044	
Formic .	00316	0.0131	00335	0.015	0.039
Acetic .	00083	0.0034	00088	0.004	0.0123
Monochloracetic .	01036	0.0430	01059	0.048	0.07
Dichloracetic .	0556	0.2304	0593	0.271	0.33
Trichloracetic .	1645	0.6820	1647	0.754	0.80
Oxalic .	0421	0.1746	0400	0.186	0.24
Tartaric .	0055	0.0229			0.05

The columns II., IV., and V. certainly do not absolutely agree, but the constants which they attribute to each acid are of the same order of magnitude and in many cases are tolerably close—which is all the more remarkable since these constants are derived by very diverse operations.

The constants  $k$  have been determined by yet another means, namely, by the rapidity with which acids decompose ACETAMIDE in aqueous solution.

The reaction



gives rise to the formation of an ammonium salt, and the amount of this present at any moment can be determined by means of alkaline hypobromite.

As far as BASES are concerned, very little work has been done. However, *Ostwald* has given us a series of numbers which expresses the relative speeds with which different bases bring about the saponification of ethyl acetate in an aqueous medium. As the metallic acetate formed in the reaction exerts a retarding influence, greater or smaller according to the nature of the base, *Ostwald* has eliminated this source of irregularity by calculating for each case the *initial* coefficient of speed.

The following are his results :

Sodium hydrate	. . . 162	Amylamine . . .	18.5
Potassium „	. . . 161	Allylamine . . .	4
Lithium „	. . . 165	Dimethylamine . . .	22
Thallium „	. . . 148	Diethylamine . . .	26
Ammonia . . .	3	Triethylamine . . .	22
Methylamine . . .	19	Piperidine . . .	27
Ethylamine . . .	19	Tetraethylammonium	
Propylamine . . .	18.6	hydrate . . .	131
Isobutylamine . . .	14.4		

For the alkaline-earth bases (lime, strontia, and baryta) the constant seems to be slightly lower than that for soda



## III. HYDROLYTIC DISSOCIATION

IN the preceding chapters we have shown that each acid, and probably each base, possesses an activity peculiar to itself, and it manifests this with a constant intensity in a series of reactions. The prime cause of this behaviour is revealed to us by a study of the ELECTRIC CONDUCTIVITIES.

The following table contains the conductivities of some acids *in normal aqueous solution*,<sup>1</sup> hydrochloric acid being taken as the standard of comparison :

Hydrochloric . . . . .	1.000	Acetic . . . . .	0.0142
Hydrobromic . . . . .	1.001	Monochloracetic . . . . .	0.0490
Nitric . . . . .	0.996	Dichloracetic . . . . .	0.2530
Sulphuric . . . . .	0.651	Trichloracetic . . . . .	0.6230
Ethylsulphonic . . . . .	0.799	Oxalic . . . . .	0.1970
Benzenesulphonic . . . . .	0.748	Tartaric . . . . .	0.0228
Formic . . . . .	0.0168		

With the exception of some digressions due to the conditions of the experiment,<sup>2</sup> this series of members is absolutely similar to that given on page 250. The activity of the acids is, therefore, proportional to their conductivity, that is to say, to their degree of dissociation. Hence it seems that the activity is due only to the ionised molecules.<sup>3</sup>

<sup>1</sup> One equivalent per litre.

<sup>2</sup> Particularly to the different concentration of the solutions which are used for the experiments on saponification, inversion, neutralisation, and electric conductivity.

<sup>3</sup> We therefore measure the relative strengths of dissolved acids by their molecular conductivity, or rather by their *degree of dissociation*. It must, however, be admitted that this method of measuring the strength of acids is not of a very general character, inasmuch as it depends too greatly on the conditions of the experiment, and particularly on the dilution of the solutions examined. If we compare, for instance, hydrochloric and acetic acids, we find that in

## HYDROLYTIC EQUILIBRIUM

It has been pointed out, in speaking of the dissociation brought about by heat, that the *thermolysis* of ammonium chloride, of phosphorus pentachloride, and of some other substances, is regulated by the equation of equilibrium  $ku = k_1 u_1 u_2$ . In the majority of cases  $u_1 = u_2$ , so the equation becomes  $ku = k_1 u_1^2$ .

In the case of the dissociation of dissolved substances, we must consider that the water plays a part corresponding to the rôle played by the heat in the other dissociation.<sup>1</sup> The cause of the phenomenon is new, but the effect produced is analogous, so we are entitled to assume that for a binary electrolyte (one with two ions) the equation of equilibrium is

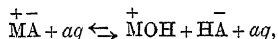
$$ku = k_1 u_1^2.$$

This equation denotes that there is a constant ratio between the product of the concentrations  $u_1$  of the ionised molecules and the concentration  $u$  of the remaining undissociated substance.

The experimental determination of the concentrations  $u$  and  $u_1$  as a rule offers no difficulty, and may be carried

normal solution the two acids are very unequally dissociated, whilst in extremely dilute solution they have the same degree of dissociation.

<sup>1</sup> The solution of one molecule of salt gives rise to the reversible reaction



in which the active mass of the water is constant. The quantity of solvent generally largely preponderates, and the disappearance or formation of a few  $\text{H}_2\text{O}$  molecules is of little consequence. In order to simplify the equation of equilibrium the influence of the solvent is taken into account in the coefficients  $k$  and  $k_1$ . (In an analogous manner the coefficients  $k$  and  $k_1$  of the thermal dissociation take into account the influence of the temperature.)

out by any of the methods by which the degree of dissociation is ascertained. The simplest way is by determining the electric conductivity.

In order to cite an example, suppose we have a solution containing one gram-equivalent of acetic acid in  $v$  litres. We know the maximum molecular conductivity (the value  $\mu_{\infty}$ , page 201) of this acid, and the molecular conductivity of the solution in question can be experimentally determined. The ratio  $\frac{\mu}{\mu_{\infty}}$  is equal to the degree of dissociation

and tells us that a fraction  $x$  of the dissolved equivalent has suffered dissociation whilst the remainder  $1-x$  of the equivalent has not been changed. The concentration  $u_1$  of the ionised molecules, that is, their number of equivalents per litre of solution, is, therefore, expressed by  $\frac{x}{v}$ , and the concentration  $u$  of the undissociated acid will be  $\frac{1-x}{v}$ .

By introducing these values into the equation of equilibrium, we get

$$\frac{k}{k_1} = K = \frac{x^2}{(1-x)v}.$$

We notice that the value of  $K$  is a function of the volume  $v$ , and this offers us a means of checking the exactness of the theory.

For acetic acid at  $25^{\circ}\text{C}$ .,  $\mu = 364$ —deduced from the molecular conductivity of sodium acetate.

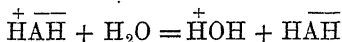
By determining the molecular conductivity of free acetic acid for a series of solutions containing one gram-equivalent in  $v, v_1, v_2, \dots$  litres, we can calculate the ratio  $\frac{\mu}{\mu_{\infty}}$  in

each case, and then we have a series of degrees of dissociation  $x, x_1, x_2, \dots$ . We might then examine if the correlative values of  $v$  and of  $x$  satisfy the equation of equilibrium.

*Ostwald* has made this study, and his results, given in the following table, show admirably the constancy of  $K$ :

V.	$\mu$	$x^+$	K
8	4.34	0.0119	0.0000180
16	6.10	0.0167	179
32	8.65	0.0238	182
64	12.09	0.0333	179
128	16.99	0.0468	179
256	23.82	0.0656	180
512	32.20	0.0914	180.
1024	46.00	0.1266	177

The equation of equilibrium for binary electrolytes, just confirmed for acetic acid, is generally applicable to monobasic acids of moderate conductivity (*Ostwald*, 1889). The equation also holds good for dibasic acids provided the dissociation does not reach 50 per cent. This fact shows that dibasic acids at the commencement of their dissociation behave like binary electrolytes and decompose according to the equation



Succinic acid and even sulphuric acid belong to this category. In the solutions employed by *Thomsen* the sulphuric acid was not dissociated to a greater extent than 50 to 60 per cent., and this explains its comparatively low avidity: it would react as  $\overset{+}{\text{H}}\text{SO}_4\text{H}$  so, that a half gram-molecule, from the point of view of avidity, would only be equal to a half-equivalent.

For binary electrolytes of high conductivity, neutral salts, inorganic acids and bases, the application of the equation of equilibrium leads to irregularities. For tertiary

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\* We see that the dilution and the degree of dissociation increase simultaneously. The reason of this is, that by the addition of water the active mass of the dissociating agent is increased.—We see besides that an increase in the volume of the solution diminishes the value of the ratio  $\frac{2c_1^2}{u}$  in such a way that the equilibrium can only be re-established by an increase in the dissociation.

electrolytes the experimental confirmation of an equation of equilibrium is still wanting.<sup>1</sup>

### THEORY OF ISOHYDRIC SOLUTIONS

The following question has been attacked by *Arrhénius*: What conditions must be fulfilled in order that no disturbance of the equilibrium take place when two solutions are mixed? The most interesting case is that of the mixture of two solutions one of which at least is only imperfectly dissociated, and both of which contain a common species of ionised molecule; for example, two acid solutions containing

basic water  $\overline{\text{HOH}}$ , two base solutions containing  $\overline{\text{HOH}}$ , or solutions of salts derived from the same acid or from the same base. Experiment and theory both show that the equilibrium of dissociation only persists after mixing, if the common ionised molecules have the same concentration in the original solutions. Such solutions are said to be *isohydric*.

The theoretical deduction of this law offers no difficulty. Suppose we have a solution of acetic acid characterised by the equation of equilibrium

$$Ku = u_1^2,$$

and a solution of sodium acetate, for which

$$cw = w_1^2.$$

In order that these two solutions may be isohydric, the ionised molecules  $\overline{\text{C}_2\text{H}_3\text{O}_2\text{H}}$  must have the same concentration in both solutions; consequently,  $u_1 = w_1$ . After mixing 1 litre of the first solution with 4 litres of the second, the concentration of the molecules  $\overline{\text{C}_2\text{H}_3\text{O}_2\text{H}}$  will

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<sup>1</sup> The constants  $\kappa$  are in harmony with the relative strength of the corresponding acids. But they are evidently not at all proportional to this strength. Besides, this new *measure of affinity* suffers by being applicable only to a certain category of substances, especially to binary electrolytes of moderate conductivity (organic acids, &c.).

evidently not be modified. The concentration of the unitary molecules  $C_2H_3O_2$  and of the  $\overset{+}{H}OH$  molecules will be reduced to a fifth, that of the unitary molecules  $C_2H_3O_2Na$  and of the  $NaOH$  to four-fifths of the original value. Now the equations

$$K \frac{u}{5} = u_1 \frac{u_1}{5}$$

$$C \frac{4w}{5} = w_1 \frac{4w_1}{5}$$

show that the acetic acid and the sodium acetate continue to be in equilibrium with their products of hydrolytic decomposition. There is, therefore, neither any further dissociation nor a reunion of the dissociated molecules, and the electric conductivity of the mixed solution will be equal to  $\frac{1}{5}$  that of the acetic acid solution plus  $\frac{4}{5}$  that of the sodium acetate solution. It is evident that, instead of taking 4 litres of the sodium acetate solution, we might have taken any amount of it and we should always arrive at an analogous result.

By the mixture of heterohydric solutions (in which  $u_1 \geq w_1$ ), the equilibria are disturbed and reactions take place. The reader may easily be convinced of this by following an example.

Two acid solutions are isohydric when the molecules  $\overset{+}{H}OH$  contained in them have the same concentration. It is now expedient to apply ourselves to a practical example, and ascertain the degree of dilution of a hydrochloric acid solution which would be isohydric with a solution of one equivalent of acetic acid in 8 litres of water. For this acetic acid solution the degree of dissociation is 0.0119 (page 255): in 1 litre there is, therefore,

$$\frac{0.0119}{8} = 0.0015 \text{ equivalent}$$

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$$\frac{0.0119}{8} = 0.0015 \text{ equivalent}$$

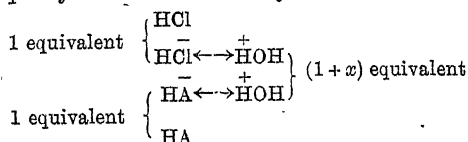


of each of the ionised molecules  $\text{C}_2\text{H}_3\text{O}_2\text{H}$  and  $\text{HO}^\oplus\text{E}$ . The hydrochloric acid must be considered as totally dissociated into  $\text{H}^\oplus\text{Cl}^-$  and  $\text{HO}^\oplus\text{H}$ . In order that the common molecules  $\text{HO}^\oplus\text{H}$  should have the same concentration in both solutions, one equivalent of hydrochloric acid must be dissolved in such a volume of water that  $\frac{1}{V} = 0.0015$ , that is, in 667 litres.

#### AVIDITY AND DEGREE OF DISSOCIATION

It has already been pointed out that the *avidity* of acids is proportional to their degree of dissociation, and seems to depend only on the ionised molecules. In other words, the degree of activity with which an acid ionises molecules of water is the same as that which it exercises when brought into contact with molecules of a basic nature. In the case of the action of two acids on one base, the acid with the greater ionising power will also have the greater action on the base.

But we may try to study this question in a more thorough manner. In a solution containing one equivalent of hydrochloric acid and one equivalent of a weak acid HA (acetic acid, for example), these two electrolytes are unequally dissociated: the system

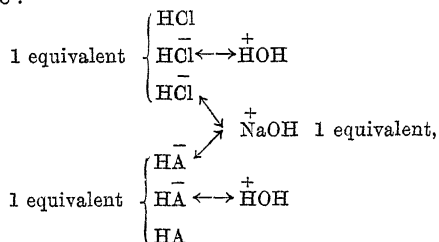


contains few unitary molecules HCl and many H<sup>+</sup> molecules.

Suppose now that one equivalent of caustic soda takes the place of a corresponding quantity of ionised water

<sup>1</sup> By the reaction

The part played by the base towards one or the other acid is a matter of indifference, because the sodium salts must be considered as completely dissociated. We shall then have :



and in this system the equilibrium depends on the quantities of the two acids remaining in the state of simple aqueous solution. In order that these remaining parts may not in any way change the equilibrium established, they must have the same activity or force ; that is to say, they must react by means of the same number of ionised molecules and be *isohydric*.

If HA represents acetic acid and if the total volume of the solution is 7 to 8 litres, the remaining parts of the two acids must be in the proportion of about 0.0015 (HCl) to 0.9985 (acetic acid).<sup>1</sup>

To account for these facts *Thomsen* says : When there is competition between one equivalent of hydrochloric acid and one equivalent of acetic acid for one equivalent of caustic soda, the acids unite with quantities of the base which are in the proportion of 0.9985 (or 1) to 0.0015. It would be better to say : the remaining quantities of the acids, that is, the parts which continue to behave simply as substances dissolved in water, are in the proportion of 0.0015 to 0.9985. These two statements may appear to be identical ; they are, however, very different. Only the latter is in conformity with our theories, and it alone

<sup>1</sup> See the calculation on p. 257.

permits us to speak without too many mental restrictions of dissociation of salt molecules into free ionised molecules.

*Remark.*—It is quite evident that all this might be equally well interpreted by the theory of free ions. But I consider *Arrhenius's* hypothesis to be rather unsatisfactory, and I have endeavoured to show that it is not indispensable.

# APPENDIX

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## ON THE DISSOCIATING ACTION OF ORGANIC SOLVENTS<sup>1</sup>

THE reader is aware that in most cases a distinction must be drawn between the constitutive particle of a substance and its molecule. The former is often a multiple of the latter, and that not only for solid or liquid<sup>2</sup> substances but also for certain vapours.<sup>3</sup>

The solution of a substance is generally accompanied by a dislocation of the molecular groupings, and eventually also by a dissociation of the salt molecules. But, from the point of view both of the isolation of the molecules and of the dissociation of the same, it is not necessary that all solvents should manifest the same degree of activity.

If we estimate this activity *from a study of the boiling or freezing points* of solutions, the result of the investigation is : *Water* is the disintegrating agent *par excellence*; it not only breaks down almost all substances to simple molecules, but it

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<sup>1</sup> This subject might well have been treated of directly after the chapter on the nature of salt solutions. But as it is rather long and detailed it might, at that point, disturb the simplicity and the order of the theoretical statements, and I prefer rather to insert it here as a *postscript*.

<sup>2</sup> *Ramsay* and *Traube* have proved this. In the liquid state molecular association is very frequent; in the solid state it is the rule and not the exception.

<sup>3</sup> Abnormal density of acetic acid at a temperature just above its boiling point.

also very energetically dissociates electrolytes. Some other solvents are, to a certain degree, possessed of the same properties as water, inasmuch as they have the power of isolating the molecules of dissolved substances; but they exercise only a very weak dissociating action, or none at all,<sup>1</sup> on electrolytes. To this category belong the lower members of the series of organic alcohols and acids, and also some substances which contain no hydroxyl, such as ketones, nitroethanes, and nitriles. The hydrocarbons, nitrobenzene, ethylene bromide, chloroform, carbon disulphide, and some other organic liquids employed in boiling and freezing point determinations, have only a very weak disintegrating action, and in some cases they even allow the dissolved substance<sup>2</sup> to remain in the state of double or multi-molecules.

Such are the results furnished by the *indirect osmotic methods*. But we must notice that a certain number of the liquids mentioned are able to dissolve some electrolytes and thus form solutions which conduct fairly well; hence it would be desirable to submit these first results to an *electro-chemical investigation*.

For *aqueous* solutions the factor  $x$ , which denotes the degree of dissociation of the dissolved substance, is, as we have already seen, independent of the method by which it is arrived at;<sup>3</sup> and, indeed, we have taken this agreement as the principal confirmation of our theories on the constitution of salt solutions.

But in the case of solutions *in an organic solvent*, it very often happens that this agreement no longer exists and that the value found for  $x$  by the boiling-point method is lower than its electro-chemical value. And in face of this disagreement between the two  $x$ 's, our theoretical conceptions seem to be rather compromised.

Amongst organic solvents of a more or less dissociating power, a certain number of alcohols, ketones, and nitriles have

<sup>1</sup> N.B.—We confine ourselves here to indications given by osmotic methods. We shall find later that a correction must be introduced.

<sup>2</sup> Namely, alcohols, phenols, certain organic acids, &c.

<sup>3</sup> By boiling or freezing point method  $x = \frac{i-1}{n-1}$ ; electro-chemically  $x = \frac{\mu_2}{\mu_\infty}$ .

been studied. For the lowest members of these series *G. Carrara* and *P. Dutoit*<sup>1</sup> have discovered the following facts:

a. If we consider only the data obtained from the *boiling points*, the dissociation is very small in methyl alcohol solution and almost nil in acetone solution.<sup>2</sup>

b. From the *electro-chemical point of view*, the opposite is the case—methyl alcohol, acetone, and acetonitrile have a fairly powerful dissociating action. For, in *very dilute solution*, it frequently happens that the conductivity  $\mu_v$  or  $\mu_\infty$  of the dissolved substance is as great in the organic solution as in aqueous solution, or even greater.<sup>3</sup> It is true that *at moderate dilution* water has by far the greater dissociating power, and that a methyl alcohol or acetone solution is generally a much poorer conductor than an aqueous solution of the same concentration.<sup>4</sup> Yet the fact remains that organic liquids may give solutions which are good conductors, that is to say, highly dissociated solutions, and consequently the two methods of investigation *a* and *b* seem to contradict each other.

To show that this contradiction is only apparent, we shall go a little deeper into the matter and consider the following:

1. As far as the disintegration of a dissolved substance is concerned, it is necessary to distinguish between the *decomposition* of the molecular aggregates and the *dissociation* proper.

<sup>1</sup> *G. Carrara*, 'Gazz. Chim. Ital.' 26, i. 119, and 27, i. 207; *P. Dutoit and Aston*, 'Comptes Rendus,' 125, 240; *Dutoit and Friderich*, 'Bull. de la Soc. Chim.,' 19, 321.

<sup>2</sup> In acetone solution *Dutoit and Friderich* have found the normal molecular weight by the boiling-point method for the salts:  $\text{NCSNH}_4$ ,  $\text{NaI}$ ,  $\text{LiCl}$ ,  $\text{HgCl}_2$ ,  $\text{CdI}_2$ .

<sup>3</sup> This high conductivity has been found by *Carrara* in methyl alcohol solution for certain neutral salts, such as  $\text{N}(\text{CH}_3)_4\text{I}$ , and  $\text{S}(\text{C}_2\text{H}_5)_3\text{I}$ , and in acetone solution for the salts:  $\text{KI}$ ,  $\text{NaI}$ ,  $\text{NH}_4\text{I}$ ,  $\text{N}(\text{CH}_3)_4\text{I}$ ,  $\text{S}(\text{C}_2\text{H}_5)_3\text{I}$ . According to *Dutoit and Friderich*, the conductivity  $\mu_\infty$  of  $\text{AgNO}_3$  and  $\text{NaI}$  in acetonitrile solution is much greater than in aqueous solution.

For  $\text{HCl}$  and  $\text{CCl}_3\text{CO}_2\text{H}$ , as also for the free alkalis  $\text{KOH}$ ,  $\text{N}(\text{CH}_3)_3\text{OH}$ , &c., the conductivity  $\mu_\infty$  is much lower in methyl alcohol than in water. In acetone solution the conductivity of the acids mentioned has been found to be very low (*Carrara*).

The tertiary electrolytes  $\text{HgCl}_2$  and  $\text{CdI}_2$  have, in acetonitrile solution, a very low conductivity (*Dutoit*).

<sup>4</sup> At moderate dilution, in order that the dissolved substance attain a certain degree of dissociation, the methyl alcohol or acetone

In aqueous solution this first action seems quite generally to be completely accomplished, and the second proceeds to an extent which depends on the nature of the dissolved substance and on the dilution. But in another solvent, such as methyl alcohol, acetone, or acetonitrile, it is possible that the decomposition only occurs after the dissociation, and that the latter is, at least partially, exercised on the complex particles. If this supposition be true, then the electrolytic decomposition of a salt  $M_2R_2$ <sup>1</sup> does not always take place in the same manner. In aqueous solution the decomposition precedes the dissociation and the simplified molecules  $\overset{+}{M}\overset{-}{R}$  give the ions  $\overset{+}{M}$  and  $\overset{-}{R}$ . In organic solvent solution, on the contrary, the substance might be only slightly decomposed and behave as if it were constituted of the ions  $\overset{+}{M}$  and  $\overset{-}{R_2M}$  (or  $\overset{-}{R}$  and  $\overset{+}{M_2R}$ ).<sup>2</sup>

2. The organic solvents capable of forming conducting solutions are generally characterised by a more or less pronounced reactivity.<sup>3</sup> This is quite evident in the case of the alcohols, phenols, acids, and other substances of the water-type. It is less so, yet not less real, for certain liquids which contain no hydroxyl but typical hydrogen atoms replaceable by metals or organic radicals: such are acetone,<sup>4</sup> nitroethane,<sup>5</sup> and acetonitrile.<sup>6</sup>

Let us now pass on to the difficulty referred to above, and let

<sup>1</sup> For crystalline salts it has been shown that the particle is often bimolecular.

<sup>2</sup> For a given electrolyte the speed of the ions does not require to be the same in different solvents, for not only is the composition of the ions subject to variation (as here shown), but their ease of transportation may be influenced by the degree of viscosity of the solvent.

<sup>3</sup> It may be added that they are also characterised by a high association factor (*Ramsay, Traube*) and by a large dielectric constant (*Nernst*). On the dielectric constant see *Nernst's* publications ('*Berichte der königlichen Gesellschaft der Wissenschaften in Göttingen*,' 1893), and those of *Drude* ('*Zeitschrift für physik. Chem.*,' 23).

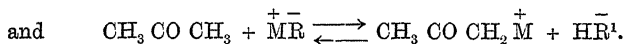
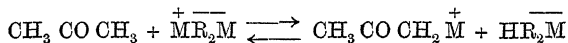
<sup>4</sup> In the ketones the hydrogen atoms attached to the carbon next to the CO group play this particular part, as *Claisen* has shown.

<sup>5</sup> Nitroethane has the character of an acid and forms salts which can be isolated.

<sup>6</sup> The polymerising action of sodium on nitriles seems to be due to the transitory formation of metallic derivatives (see *V. Meyer and Jacobson's* '*Organische Chemie*,' p. 299).

us take, for example, an acetone solution of a salt  $M_2R_2$ ; and for the sake of simplicity of expression we shall meantime accept the hypothesis of *free ions*. If we consider, in the first place, a fairly concentrated solution, we can imagine that what would take place would be this: A complex equilibrium would be established between particles  $M_2R_2$ , molecules  $MR$ , and the products of dissociation  $\overset{+}{M}$  and  $\overline{R_2M}$ ,  $\overset{+}{M}$  and  $\overline{R}$ . And, if the decomposition is kept back by the dissociation taking place first, the ions  $\overset{+}{M}$  and  $\overline{R_2M}$  will predominate in the mixture. We see then that the boiling-point of such a solution may indicate the normal molecular weight (since  $MR$  is the arithmetic mean of  $M$  and  $R_2M$ ), whilst the electric conductivity denotes that quite a large dissociation has taken place. If we now consider a very dilute solution, we see that there can be no conflict between the two  $x$ 's because in this case the boiling-point method is not applicable, and we must fall back on the electro-chemical method which indicates that the dissociation is pretty far advanced and points to the predominating or exclusive presence of the ions  $\overset{+}{M}$  and  $\overline{R}$ .

~~In~~ the hypothesis of *ionised molecules* the reactivity of acetone may be accounted for by the transpositions:



Of these two reversible reactions the first predominates in concentrated solution and the other in dilute solution. Both lead to a stationary equilibrium, on account of which the ions possess a certain mobility and the solution an electric conductivity. For the rest, the interpretation given above does not require to be modified.

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<sup>1</sup> According to the first reaction the material of the particle  $\overline{M_2R_2}$  is distributed between two molecules, and the molecular weight (by the boiling-point) would be normal. The molecule  $\overline{HR_2M}$  is similar to certain acid salts, such as  $KF_2H$ ,  $K(C_2H_3O_2)_2H$ .



If the solvent considered had been methyl alcohol or acetonitrile, the typical hydrogen atom, endowed with the reactivity, would have been in the former case the hydrogen of the hydroxyl, in the latter case a hydrogen attached to the carbon atom next to the CN group.

TABLE OF ATOMIC WEIGHTS

Elements		Atomic weights	Elements		Atomic weights
Hydrogen .	H	1.0075	Zirconium .	Zr	90.5
Helium .	He	4 (?)	Niobium .	Nb	94.0
Lithium .	Li	7.03	Molybdenum .	Mo	96.0
Beryllium .	Be	9.1	Rhodium .	Rh	103.0
Boron .	B	10.95	Ruthenium .	Ru	101.7
Carbon .	C	12.001	Palladium .	Pd	106.5
Nitrogen .	N	14.045	Silver .	Ag	107.93
Oxygen .	O	16.0	Cadmium .	Cd	112.1
Fluorine .	F	19.05	Indium .	In	114.0
Sodium .	Na	23.050	Tin .	Sn	119.0
Magnesium	Mg	24.36	Antimony .	Sb	120.0
Aluminium .	Al	27.1	Tellurium .	Te	127.5
Silicon .	Si	28.4	Iodine .	I	126.86
Phosphorus	P	31.0	Cæsium .	Cs	132.9
Sulphur .	S	32.06	Barium .	Ba	137.4
Chlorine .	Cl	35.455	Lanthanum .	La	138.5
Potassium .	K	39.14	Cerium .	Ce	140.0
Argon .	A	39.9 (?)	Praseodymium	Pr	140.5 (?)
Calcium .	Ca	40.0	Neodymium .	Nd	143.5 (?)
Scandium .	Sc	44.0	Samarium .	Sm	150.0
Titanium .	Ti	48.17	Gadolinium .	Gd	156.0 (?)
Vanadium .	V	51.4	Terbium .	Tb	160.0 (?)
Chromium .	Cr	52.14	Erbium .	Er	166.0 (?)
Manganese .	Mn	55.0	Decipium .	Dp	170.7 (?)
Iron .	Fe	56.0	Ytterbium .	Yb	173.0
Nickel .	Ni	58.7	Tantalum .	Ta	183.0
Cobalt .	Co	59.1	Tungsten (Wolfram)	W	184.4
Copper .	Cu	63.6	Osmium .	Os	190.8
Zinc .	Zn	65.4	Iridium .	Ir	193.0
Gallium .	Ga	70.0	Platinum .	Pt	195.2
Germanium	Ge	72.5	Gold .	Au	197.3
Arsenic .	As	75.0	Mercury .	Hg	200.0
Selenium .	Se	79.0	Thallium .	Tl	204.15
Bromine .	Br	79.96	Lead .	Pb	206.92
Rubidium .	Rb	85.44	Bismuth .	Bi	208.0
Strontium .	Sr	87.6	Thorium .	Th	233.0
Yttrium .	Y	89.0	Uranium .	U	240.0

*Remarks.*—1. The basis of this table is :  $O = 16$ . This is the most practical arrangement, because almost all the atomic weights have been determined with relation to oxygen. If the weight-relation  $O/H$  were exactly known (unfortunately, it is extremely difficult to exactly establish it), then the basis of the table might be taken  $H = 1$ , as being preferable from the theoretical point of view. In the first part of this book we have frequently made use of atomic (and molecular) weights calculated for  $H = 1$ , and these are consequently slightly smaller than those given in the table.

2. The existence of some of the elements whose atomic weights lie between 140 and 173 is still more or less problematic.

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#### BIBLIOGRAPHICAL NOTE

Besides the numerous *periodicals* the following works have been consulted in the preparation of this book : The works on theoretical chemistry by *Wurtz*, *Lothar Meyer*, *Ostwald*, and *Nernst* ; on thermo-chemistry by *Berthelot* and *Thomsen* ; on thermodynamics by *Planck* ; on electro-chemistry by *Le Blanc* ; and on practical physical chemistry by *I. Traube*, *Ostwald*, and *Biltz*.

The book ' *Die mathematische Behandlung der Naturwissenschaften* ' by *Nernst and Schönflies* is strongly recommended to students.

# ATION

Solid	Dissolved	Solid	Dissolved
118.1	114.5	30.1	27.2
		67.1	64.2
110.7	110.1	22.6	22.1
		59.5	59.0
	115.8	2.3	-2.1
88.0	86.5		89.35
			84.7
218.4			$x + 41.8$
225.8		93.8	83.8
+ 95.5	$x + 93.4$	84.8	79.2
210.7		113.5	101.4
	155.5	100.3	96.8
	127.1		86.8
	335.1	84.3	74.4
	120.8	126.1	120.1
	122.2		107.7
	140.0	454.5	440.0
	123.5	273.2	274.6
		261.4	263.9
	89.6	256.3	258.0
	558.0	278.8	285.3
107.6		233.3	228.0
	52.0	270.8	276.4
		227.0	222.7
		205.3	199.0
		269.1	precipit'd.
		270.5	Calcspar
23.2	26.6	270.8	Aragonite
			88.9
-9.8		175.7	179.0
-7.25		170.3	174.4
9.9		344.4	
		ate	

pat of formation of  
q, HCl aq) are added

$$a) - (H_2, O) = (x +$$



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